SYNTHESIS AND CHARACTERIZATION OF BIODIESEL USING WASTE COOKING OIL AND CALCIUM OXIDE FROM WELDERS SLURRY

BY

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DEPARTMENT OF CHEMISTRY

AHMADU BELLO UNIVERSITY, ZARIA

Cover Page

AUGUST, 2016

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DEPARTMENT OF CHEMISTRY,
FACULTY OF SCIENCE
AHMADU BELLO UNIVERSITY, ZARIA
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Title Page

AUGUST, 2016

DECLARATION

I declare that this work intitled 'Synthesis and Characterization of Biodiesel using Waste Cooking Oil and Calcium Oxide from Welders Slurry' has been performed by me in the Department of Chemistry, under the supervision of Professor V.O Ajibola and Professor E.B Agbaji. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this research was previously presented for another degree or diploma at any university or institution.

Michael Terungwa Abatyough

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Name of Student Signature Date

CERTIFICATION

This Dissertation titled SYNTHESIS AND CHARACTERIZATION OF BIODIESEL USINGWASTE COOKING OIL AND CALCIUM OXIDE FROM WELDERS SLURRYby Michael Terungwa ABATYOUGH meets the regulation governing the degree of MASTER OF SCIENCE IN ANALYTICAL CHEMISTRY of Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

_____ _____

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DEDICATION

This Dissertation is dedicated to God Almighty.

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ABSTRACT

Waste materials (carbide slurry and waste cooking oil) were explored in esterification and trans- esterification reactions as a viable alternative to conventional resources in lowering the cost of biodiesel production. Physicochemical study suggested esterification pretreatment for the waste cooking oils (WCO), having 3.6% moisture and sediment content and acid value of 3.8 mgKOH/g. Calcium Oxide catalyst was prepared from carbide slurry by thermal activation. The Fourier transformed infrared spectroscopy (FTIR), Atomic absorption spectroscopy (AAS) and Scanning electron microscope (SEM) techniques showed that the prepared calcium oxide had improved basic sites, calcium content and surface morphology respectively. Alkali supported on calcium oxide catalyst was then prepared by wet-impregnation method. The optimization of the esterification process for waste cooking oil was carried out using $AlCl_3$ and H_2SO_4 catalysts. Using a two level, three factorial (2^3) experimental design, eight experiments were carried out at varying conditions of catalyst loading, reaction time and methanol- oil molar ratio. Response surface plot were used to show the interaction of the factors as they affect the percentage free fatty acid reduction. Free fatty acid reduction above 90% was achieved with both catalysts. Transesterification was then carried out with the esterified oils using prepared NaOH/CaO catalyst to synthesize the biodiesel. The quality and yield of the produced biodiesel was compared with those of aluminum chloride ($AlCl_3$) and alkali (NaOH) catalysts. The percentage yields of prepared biodiesels were 90.2±0.57 for $AlCl_3$, 89.7±0.16 for NaOH and 92.22±0.31 for NaOH/CaO catalyzed transesterification reactions. Fuel properties such as cetane number, cloud and pour points etc. showed trend with levels of saturation in transesterified oils. The fatty acid profile showed C16:0, C14:0, C18:0, C18:1, and C18:2. (Palmitic acid, myristic acid, stearic acid, oleic acid, and linoleic acid) to be the major fatty acids among the biodiesel samples. The reusability of the NaOH/CaO catalyst was studied and found to give an appreciable yield of 74.5 % on the fourth reaction cycle, making it a durable catalyst for biodiesel production.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
ANOVA	Analysis of Variance
ASTM	American Standard for Testing and Materials
FAME	Fatty Acid Methyl Esters
FFA	Free Fatty Acid
FTIR	Fourier Transform Infrared
GC-MS	Gas Chromatography Mass Spectroscopy
IV	Iodine Value
LDA	Linear Discriminant Analysis
NARICT	National Resarch Institute for Chemical Technology
PCA	Principal Component Analysis
PLS	Partial Least Square
SEM	Scanning Electron Microscope
SV	Saponification Value
USLD	Ultra low Sulphur Diesel
WCO	Waste Cooking Oil

CHAPTER ONE

1.0 Introduction

1.1 Biodiesel

Industrialization processes have continued to grow globally in line with human population leading to the growing worldwide demand for petrochemical resources, coal and natural gases. This phenomenon has caused the depletion of fossil energy resources to increase exponentially with consequent environmental problems to the society (Abdullah *et al.,* 2009). In the last decade, many fuel developers have shown interests in alternative renewable fuels to substitute or compliment petroleum-based fuels. An alternative fuel should be easily available, environment friendly and techno-economically competitive (Sharma *et al.,* 2008)**.**

Biodiesel is considered as a "direct-pour" alternative fuel to petroleum diesel, as it requires almost no modification to most modern diesel engines. Biodiesel can be produced locally and therefore reduces foreign oil dependence. It has been reported that biodiesel combustion can result in less air pollutants such as carbon monoxide, sulphur dioxide, particulate matter, hydrocarbons, but with slightly higher nitrogen oxides (Graboski 1998). Since the feedstock of biodiesel is mostly renewable, it significantly reduces carbon dioxide emission during its whole life cycle (Sheehan *et al.,* 1998)**.** According to the American Standard Testing Methods (ASTM),Biodiesel is defined as mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats which conform to *ASTM* D6751 specifications for use in diesel engines.(Knothe, *et al.,*2007)As an alternative fuel, biodiesel can be used in neat form or mixed with petroleum-based diesel. Biodiesel as an alternative fuel has many merits. It is derived from a renewable resource, thereby relieving reliance on

petroleum fuel imports. It is biodegradable and non-toxic. Compared to petroleum-based diesel and has a more favourable combustion emission.

1.2 Feedstock for Biodisel Production

Though biodiesel production has currently not been commercialized worldwide due to high cost of feed stock (Yun and Mahiran, 2011; Canakci and Sanli, 2008), the cost of biodiesel can be reduced by low quality feed stock such as waste or used vegetable oils, non-edible oils, trapped greese and soap stock (by-product of vegetable oil refinery) which are cheaply available and can be regarded as attractive feedstock for biodiesel production. (Ali *et al.*, 2002; Ali and Cuppett, 1995; Jian – xun, 2007; Sanli *et al*., 2008) Even though the cost of biodiesel production may be reduced, using such cheap feed stocks usually have the problem of high free fatty acid (FFA) in oil samples. These productions therefore, require a two-step process. FFA must first be converted to their methyl esters (biodiesel) via esterification using a catalyst preferably acid prior to transesterification with a homogeneous base catalyst. In the first step, FFA must be typically esterified to an acceptable level, (acid level less than one) in order to prevent soap formation and increase the biodiesel yield in the subsequent alkaline catalyzed transesterification. Usually catalysts are used to enhance such reactions.

1.3 Catalysts in Biodiesel Production

Esterification and transesterification of free fatty acids use catalysts to enhance the reaction rate. Catalysts that are commonly used in esterification include strong liquid mineral acids, heterogenous catalysts and enzymes e.t.c. Homogenous catalysts are widely used, but their reaction with free fatty acids affects the properties and yield of biodiesel. However heterogeneous catalysts have proved to be bettercompared to homogenous catalysts, due to their benefits not only in the purity of the secondary product glycerin, but also because it simplifies down streaming separation process, since it does not need much washing or

neutralization. Particulate heterogeneous catalysts can be readily separated from the products following reactions allowing the catalyst to be reused, thereby generating less waste, and consuming less energy. Recycling and reactivating the catalyst have been studied and found to maintain efficiency for use in industries (Park, 2010)**.** Researchers like, liu et al., 2010 and Ghiasi and malekzadeh, 2012 have introduced heterogeneous catalyst for their experiment, examples are CaO, SrO, BaO, and $Ca(OCH_3)_2$. However, homogeneous catalysts have been widely used in industries and they include KOH, NaOH, and CH_3ONa (Lu *et al*., 2009). Alkali metal hydroxides or alkoxides can be used as transesterification catalysts. Hydroxides are cheaper than alkoxides, but must be used in higher concentrations to achieve good reaction (Freedman *et al.*, 1984).

1.4 Statement of Problem

Globally, virgin oils are the major feedstock used for biodiesel production (Thamsiroj and murphy, 2009). This causes an imbalance in the utilization of energy sources and thus contributes to the higher cost of biodiesel feedstock (Mohammed and Ali, 2002). Also, the use of base catalyst, which is expensive, for esterification and transesterification leads to the production of soap as side reaction which, affects the quality of the biodiesel produced (Tat and van Gerpen, 2000). However, the difficulty in recovering homogenous alkali catalysts after transesterification also leads to higher cost of biodiesel production as large quantities of water and reagents are needed to purify the produced biodiesel (Dennis *et al.*, 2010).

1.5 Justification of Research

Increasing uncertainty about global energy production and supply, environmental concerns due to the use of fossil fuels, and unsustainable nature of petroleum products gives reasons for the search for alternatives to fossil fuels. (MacLeana and Laveb, 2003;; Körbitz,1999). Biodiesel is one of the best substitutes for petrodiesel due to its advantage of

environmentally friendly properties. (Helwani *et al.,* 2009). Currently, more than 95% of the world biodiesel is produced from edible oil. However, continuous and large-scale production of biodiesel from edible oil has become an issue of great concern because of competition with food materials (Mustafa, 2011; Arjun *et al.,* 2008). The most common methods for biodiesel preparation are homogenous base or acid catalyzed transesterification (Meher*et al.,* 2006).These methods, however, come with a lot of disadvantagessuch as soap formation, reduced yields of biodiesel, high cost and also their inability to be recycled. (Sharma *et al*., 2008). In this sense, methods that permit minimizing the costs of the raw materials are of special interest. The use of waste cooking oil, instead of virgin oil, to produce biodiesel reduces the raw material cost because waste cooking oil is estimated to be about half the price of virgin oil (Zheng *et al.,* 2006).The local production of heterogenous catalysts such as calcium oxide (CaO) to be used directly in biodiesel production or as solid support for other catalysts will help to reduce the overall cost of biodiesel production. This will significantly enhance the economic viability of biodiesel production in Nigeria, where this resourceabound.

1.6 Aim and Objectives

The aim of the study is to find a potential way to reduce the cost of biodiesel production by using waste cooking oil (WCO) as biodiesel feedstock as well as using calcium oxide derived from waste carbide slurry as support for the catalyst sodium hydroxide

The objectives of this research include :

(i) Pretreatment of waste cooking oil (WCO)

(ii) Purification of calcium oxide catalyst (CaO) from waste carbide slurry.

(iii) Determination of physicochemical properties of waste cooking oil (WCO)

(iv) Determination of physicochemical properties of calcium oxide catalyst (CaO) from waste carbide slurry.

(v) Esterification of waste cooking oil using aluminum chloride ($AlCl_3$) and sulphuric acid (H_2SO_4) catalysts using different reaction conditions.

(vi) Transesterification of waste cooking oil using alkali supported on calcium oxide (NaOH/CaO), aluminum chloride ($AlCl_3$), and alkali (NaOH) catalysts.

(vii) Determination of fuel properties of the biodiesel produced using NaOH/CaO, $AlCl_3$and NaOH and comparing them with the standards.

CHAPTER TWO

2.0 Literature Review

2.1 Background and History of Biodiesel

Biodiesel was first suggested for use as a means for automotive power by the inventor of the diesel engine himself, Rudolf Diesel. On April 13, 1912 Diesel proclaimed that, through vegetable oils "Motive power can still be produced from the heat of the sun, and it will always be available, even when the natural stores of solid and liquid fuels are completely exhausted" (Pahl, 2005). Early patents relating to the use of alkyl esters began to appear in 1980 (Mittelbach, 2004). In 1981 and 1982, researchers in South Africa, Germany, and New Zealand were studying the use of vegetable oil esters in diesel engines (Mittelbach, 2004).

2.2 Biodiesel Feedstock

The feedstocks used in the production of biodiesel vary. The most common feedstock include vegetable oils (soybean, palm, peanut, rapeseed, sunflower, coconut), trap grease and animal fats (tallow). Vegetable oils include edible and non-edible oils (Pinto *et al*., 2005., Montefri *et al.*, 2010; Altun, 2011). The use of animal fats, waste grease and waste cooking oils give more attractive prices, but edible vegetable oils still dominate the production of biodiesel throughout the world; Large amounts of these non-edible oil plants are available in nature and can be utilized for biodiesel production (Knothe 2005).

Available data has shown the estimated amounts of waste cooking oil (WCO) in some countries. The total waste cooking oil (WCO) potential in the EU-27 is 3.55 million tonnes, which is equivalent to 8 litres of WCO per capita, The contribution of the domestic sector is 1.748 million tonnes per year, of which it is estimated that over 60% is disposed of improperly(Rec Oil, 2013). Outside the EU, the total potential of collectable WCO from the

gastronomy sector in the assessed countries was estimated at more than 4.5 million tons(Ecofys, 2013). Unfortunately, published data from Sub-Sahara Africa is not readily available. However, given current population sizes and the large number of restaurants, hotels, road side food providers and households in Sub-Saharan cities and towns that use vegetable oils for cooking, it is conceivable that similar large quantities of waste cooking oils are beginning to grow in these countries (Zheng *et al.,* 2006).

2.3 Chemistry of Waste Cooking Oil

During frying process, oil is continuously or repeatedly subjected to high temperatures in the presence of air and moisture. Three essential degradation reactions occurs under these conditions are:

- Hydrolysis causing from the moisture content of fried food. This reaction produces free fatty acids (FFA), mono- and diglycerides.
- Oxidation causing from the contact with oxygen. Reaction products are oxidized momomeric, dimeric and oligomeric triglycerides and volatile materials such as aldehydes and ketones.
- Polymerization causing from these two reactions, and high temperatures. This reaction produces dimeric and polymeric triglycerides with ring structure (Gertz, 2000; Choe and Min, 2007).

Because of these degradation reactions mentioned above, a number of physical and chemical changes occur in frying oils including increase in viscosity, density, FFA content, total polar material (TPM), polymerized triglycerides, and decrease in smoke point, the number of double bonds, etc. If the frying process is continued, these materials will undergo further degradation and finally the oil will not be appropriate for frying. The frying oil has to be discarded.

2.4 Advantages and Disadvantages of Biodiesel

The advantages of biodiesel compared to petrodiesel ((Porteous, 2008, Gómez*et al.,* 2012) include the fact that it is a renewable energy source which is biodegradable and has much less sulphur and other pollutants, so it is environmentally friendly. However it's disadvantages include it's high viscosity which causes problems to fuel injection systems. also due to its high level of unsaturation oxidation is favoured and it is still very expensive.

2.5 Parameters Affecting the Yield of Biodiesel

Several parameters have influence in the course of the transesterification reaction. These include; reaction temperature, reaction time, molar ratio of alcohol to oil, type of catalyst, concentration, and free fatty acid content in feedstock.

2.5.1 Reaction temperature

Theconversion of transesterification is rarely influenced by temperature fluctuations so long asthe temperature remains between 20 and 70°C.by operating above the optimum temperature, the saponification of triglyceride occurs (Patil and Deng 2009). In most studies, the temperature is kept close to the boiling point of the alcohol. If methanol is used, the temperature applied is normally 50-65^{o}C this should be sufficient to produce high yield when the methanol to oil molar ratio is 6:1 (Knothe *et al*., 1997).

2.5.2 Reaction time

The time it takes for the reaction to go to completion largely depends on the catalyst type and the set temperature. The transesterification reaction is normally very slow at the beginning due to the immiscibility of the alcohol and oil. When the reaction is underway and conversion reaches the point where all components are miscible, the reaction proceeds very fast and typically takes 1-2 h to complete (Hoque *et al*., 2011).

2.5.3 Alcohol to oil ratio

One of the most important parameters affecting the yield of biodiesel is the ratio of alcohol to oil (Hoque *et al*., 2011). The alcohol-oil molar ratio needed to produce biodiesel stochiometrically is 3:1 However, since the transesterification is a reversible reaction, an excess of alcohol is normally used to ensure that the oil is completely converted into ester. The most common alcohol: oil ratio used is 6:1, which means alcohol is in excess. Most studies revealed that the 6:1 molar ratio of alcohol to triglyceride produced essentially complete conversion (Arzamendi *et al.*, 2008; Krawczyk, 1996). Further increase in alcohol content does not increase the yield of biodiesel significantly but does increase the cost of production (Graille, 1985). However, the ratio of alcohol to oil can be much higher, up to 15:1, when the free fatty acid content in the oil is high because, they reaction may reverse at insufficient amount of alcohol.Also an acid catalyzed esterification reaction is applied to effectively remove the free fatty acids (Kulkarni, 2006; Krawczyk 1996; Leung, 2006).

2.5.4 Catalyst type and concentration

The most common catalyst used in the production of biodiesel is NaOH or KOH (homogeneous catalysts). Freedman *et al.*,(1986) reported that the alkali catalysed transesterification is significantly faster than the acid-catalysed reaction. Also sodium methoxide was more effective than sodium hydroxide because generally a small amount of water is released during the mixing of methanol and sodium hydroxide which leads to hydrolysis. However sodium hydroxide is much less expensive than sodium methoxide. Sodium hydroxide of 0.3-0.5wt% gave maximum activity in beef tallow transesterification Higher concentration can decrease the biodiesel yield because of the direct saponification of triglycerides (Patil and Deng, 2009).Kim *et al.*, 2004, experimentally described theuse of a hetrogenous catalyst; Na/NaOH-Al_2O_3 in producing near-completion of soybeanoil methyl esters in 2 hours. The potential of biocatalysts in biodiesel production is also

attractingcontinuous attention and these catalysts have been found to perform equally wellwith their chemical-based counterparts to catalyse the methanolysis of soybean oil to achieve more than 92% methyl ester conversion (Shieh *et al.,* 2003).

2.5.5 The effect of free fatty acids

The free fatty acid (FFA) content in feedstock for transesterification reaction is one of the most important parameters. The FFA content should be lower than 1% when the base catalysed transesterification is being used. The use of vegetable oils with FFA content more than 1% with base catalysis, produces lower yields of biodiesel because of neutralisation of the catalyst by the FFA. Increasing the amount of catalyst then increases the possibility of soap formation which results in difficulty with ester glycerol separation . The effects of FFA in biodiesel production have been well studied. (Morshed, *et al.,* 2011) If the feedstock has FFA content higher than 1%, the FFA must be refined into esters, either by saponification or by a esterification reaction using catalyst.

2.6 Esterification

Esterification, as it applies to biodiesel production, is the chemical reaction by which a fatty acid, typically a free fatty acid in a degraded or used oil, reacts with an alcohol to produce an alkyl ester and water. The process differs from the transesterification reaction in that the reaction is occurring directly between the alcohol and the fatty acid molecule. The intermediate steps of cleaving the fatty acid chains from the glycerin backbone are not present. For this reason, no glycerin is produced during the esterification reaction.

The following equation(2.1) shows the basic esterification reaction with methanol. A fatty acid molecule reacts with a methanol molecule to form a methyl ester plus a water molecule (Deshmane *et al*., 2008).

$$R_1 - COOH + CH_3OH \leftrightharpoons R_1 - COO - CH_3 + H_2O \qquad (2.1)$$

FFAmethanol methyl ester water FX +P

2.6.1 The esterification of waste cooking oil (WCO)

Most of waste oil is spent cooking oil from restaurants. The oils have been thermally degraded by sustained high temperatures. They further degrade when in contact with water in the grease trap through hydrolysis (Du *et al*., 2008; Montefrio, 2010). This degradation produces molecules known as free fatty acids, which will chemically react with the typical alkaline catalysts used in base-catalyzed biodiesel reactions to form soap. Two problems result from this:

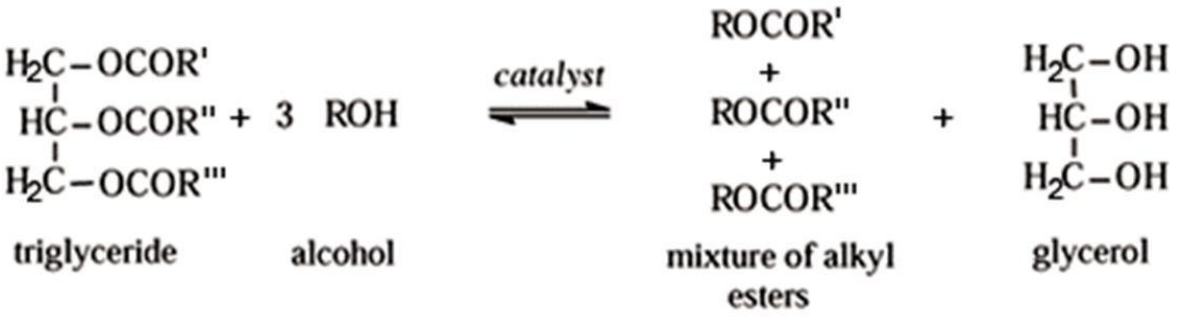
1. The catalyst is consumed resulting in either an increased catalyst imput -and therefore higher chemical costs - or an incomplete or failed reaction(Tyson, 2002).

2. soaps which are impurities in the biodiesel must be washed out (Lotero, 2005), free fatty acids are always present in oils, however mass concentrations above 4% will generate more soap than can be dealt with reasonably in a conventional base-catalyzed reaction and will prevent the reaction from going to completion in almost all cases (Tyson, 2002).

2.7 Transesterification

The chemical reaction by which a lower alcohol reacts with a tri-glyceride (oil) to yield a fatty acid alkyl ester is known as transesterification. Transesterification (also called alcoholysis) is the general term used to describe the important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety. This process is widely used to reduce the viscosity of triglycerides. When methanol is used as the lower alcohol to replace the glycerol of the triglycerides, the process is called methanolysis and fatty acid methyl esters (FAME) are formed.The overall process is a sequence of three, consecutive and reversible reactions, in which di and mono-glycerides

are formed as intermediates. The overall process of methanolysis is shown in equation 2.2 The stoichiometric reaction requires 1 mole of a triglyceride and 3 moles of the alcohol. However, an excess of the alcohol is used to increase the yield of the alkyl esters according to Le Chatelier‘s principle and to allow its phase separation from the glycerol formed.



(2.2)

According to Van Gerpen (2005), when a larger molar ratio, excess (30:1) of alcohol to oil is used the forward reaction is pseudo-first order; for a smaller molar excess (6:1) of alcohol the reaction is second-order and the reverse reaction is found to be second order. Transesterification is a reversible reaction, however in the final step when mono alkyl ester is formed; the back reaction does not take place or is very negligible because the glycerol formed is not miscible with the product, leading to a two-phase system (Van Gerpen, 2005). The transesterification reaction can take place using catalyst at lower temperatures, atmospheric pressure and lower molar excess of alcohol. For methanol and base transesterification of oil, the most commonly used temperature is 60^{o}C and the methanol to oil molar ratio is 6:1 (Van Gerpen, 2005). Among the alcohols that can be used in the transesterification process are methanol, ethanol, propanol, butanol and amyl alcohol. Methanol and ethanol are used most frequently, especially methanol because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol). Ethanol is renewable, has better dissolving potential for oils. and has much higher heating value. But

it also has slow rate of reaction and separation (Encinar *et al*., 2007; Tapanes *et al*., 2008; Zhou and Boocock, 2006).

Bio-diesel has numerous advantages over petroleum-based diesel including higher lubricity which prolongs engine life and reduces the frequency of engine component replacement, a higher cetane number and a higher flash point, meaning better and safer performance, as well as the presence of oxygen (~10%) which improves combustion and reduces CO and hydrocarbon emissions. The American society for testing and materials (ASTM standards)shown in Table 2.1 are the common standards for comparing biodiesel. These standards allow production of bio-diesel fuel of repeatable quality. The ASTM standards ensure both safety in the production of bio-diesel and quality of the end product, it's major roles include to ensure:

(i) Complete reaction to establish an equilibrium

(ii) Removal of all free fatty acids

(iii) Removal of all traces of glycerol, base catalyst and excess alcohol.

Table 2. 1: American Society for Testing and Materials (ASTM) Standards of permissible Limits

Property	Diesel	Biodiesel
Standard	ASTM D75	ASTM D6751
Composition	HC (C10- C21)	FAME (C12-C22)
Kinematic viscosity at 40^0C (mm2/s)	1.9-4.1	1.9-6.0
Boiling point (^{0}C)	188-343	182-338
Carbon weight (wt %)	87	77
Pour point (^{0}C)	-35 to -15	-15 to 16
Cloud point (^{0}C)	-15 to 5	-3 to 12
Flash point (^{0}C)	60 - 80	100 - 170
Hydrogen (wt %)	13	12
Sulphur (wt %)	0.05	0.05
Water (vol %)	0.05	0.05
Ignition quality (Cetane no)	40 - 55	48 - 60

Source: (Meher *et al.*, 2006)

2.8 Processes for Biodiesel Preparation

There are different processes which can be applied to synthesize biodiesel, the most conventional method is transesterification. Other methods include:

(i) Direct Use and Blending of Vegetable Oil

(ii) Micro-Emulsification

(iii)Thermal Cracking (Pyrolysis)

2.9 Catalyst for Biodisel Production

Catalysts are used in the estericifation process to enhance or accelerates chemical reaction process. Catalysts can be divided into two types, homogenous catalysts such as the strong

liquid mineral acids, such as H_2S0_4 and HCl e.t.c. and heterogeneous catalysts such as MgO and CaO with basic sites and mainly bronsted acid sites

2.9.1 Homogeneous catalyst

Aranda *et al.* (2007) studied acid-catalyzed homogeneous esterification reactions for biodiesel production from palm fatty acids. In their finding, small amount of catalyst (0.01% w/w) is enough to promote the reaction, with the conversion increasing with higher amounts of catalyst. The acid strength of the catalyst was responsible for the higher activity and methane sulphonic acids by releasing more H^+ species to protonate the carboxylic moiety of the fatty acid (rate determinant step). The higher polarity and shorter chain of methanol resulted in higher activity compare to ethanol and this shows the presence of steric hindrance in the reaction because of higher water inhibition which is attributed to phase miscibility and emulsion formation. Quantum chemistry studies have shown that the double bond of oleic acid increase the reactivity of carboxylic moiety of the fatty acid. Sun *et al.,* (2000) studied fractional isolation, physico-chemical characterization and homogeneous esterification of hemicelluloses from fast-growing poplar wood. The homogeneous catalysts suffer from several drawbacks, such as the existence of side reaction with reactant, corrosive nature and difficulty in the separation of catalyst from products. The alternative way to overcome these drawbacks is using heterogeneous catalyst. Solid acid catalysts are not corrosive, can be coated onto a support and easily reused. Ion –exchange resins, zeolites, sulphated zirconia and niobium acid are the examples of catalysts used in esterification reactions.

2.9.2 Heterogeneous catalyst

The heterogeneous catalyst is selected due to its activity and reusability compared to conventional homogeneous catalyst. Homogeneous catalysts have side reaction with reactant and corrosive nature that can harm the environment. This weakness of

homogenous catalysts leads the preference for heterogeneous catalysts in most experiments. Peters *et al.* (2005) concluded that, solid acid catalysis is very effective from the aspect of activity and reusability, compared with homogeneous catalysts. The activity per proton of solid acid catalysts is significantly different due to the specific reaction. Reaction rate depends on the environment of the acid sites such as hydrophobicity. The diffusion of molecules to the active sites is important in the case of porous solid acids. Chouhan and Sarma (2011), mentioned that different heterogeneous catalysts might be used for biodiesel production, including basic, acidic, mixed materials and materials generated from bio-waste. The most currently studied heterogeneous catalysts include calcium oxide, both pure, derived or supported in different materials (silica and alumina, amongst others), supported sodium, potassium, and their hydroxides, catalysts containing zirconia (ZrO), hydrotalcite ($Mg_6\ Al_2(OH)_{16}CO_3.4H_2O$), catalysts based on dolomite ($CaMg(CO_3)_2$, several other oxides such as the ones of zinc, manganese, aluminium, iron and titanium , silica/silicates based materials and zeolites. Calcium oxide, both alone or supported, seems to be the most promising catalyst, presenting higher basicity, lower solubility, acceptable reaction conditions and lower price (Dias *et al*., 2011).

Heterogeneous base/acid catalysts are thought to be very attractive for biodiesel production as a result of easy separation of reaction products and for minimizing waste formation due to neutralization of homogeneous base/acid catalysts. They could be classified as Bronsted or Lewis catalysts, though in many cases both types of the sites could be present and it is difficult to evaluate the relative importance of the two types of sites in the reaction. According to (Di Serio *et al*., 2008), the reaction mechanisms of both Bronsted and Lewis catalysts are similar to homogeneous Bronsted basic homogeneous catalysts (i.e. NaOH, KOH) unlike the case of acid catalyst. Moreover, both homogeneous (H_2SO_4, *p*-toluene

sulphonic acid) and heterogeneous Bronsted acid catalysts are active mainly in the esterification reaction whereas both homogeneous (i.e. metal acetate, metal complex) and heterogeneous Lewis acid catalysts are more active in the transesterification reaction. The formation of water in the esterification reaction can deactivate these Lewis catalysts. Reaction temperature is usually increased to produce a sufficient reaction rate in the transesterification reaction due to the lowered activity of the acid catalyst, (D'Cruz *et al*. 2007; Di Serio *et al*., 2008) revealed that, even though it is claimed that heterogeneous catalysts are insoluble, in many experiments, leaching of catalysts was observed which could be due to the presence of glycerol in the reaction.Also, both basic (anion exchange) and acidic (cation exchange) ion exchange resins have been tried as heterogeneous catalysts. In case of basic ion exchange resins ,the catalytic activity diminishes during the reactions because of exchange reactions between the resin's hydroxyl ion and triglycerides and as a result of the formation of fatty acids (Chakrabarti and Sharma, 1993).

In case of acidic resins (i.e. Amberlyst – 15) the catalytic deactivation is due to the blockage of the sites by adsorbed intermediates or product species. To be economically viable and to compete commercially with petroleum-based diesel fuel, processes for the synthesis of biodiesel need to involve continuous processing in a flow system, should have as few reaction steps as possible and limit the number of separation processes through the use of the robust heterogeneous (solid) catalyst. Appropriate solid catalysts can be easily incorporated into a packed bed continuous flow reactor, simplifying product separation and purification and reducing waste generation. Unlike homogenous catalyst, heterogeneous catalyst neither dissolves in polar alcohol nor non-polar triglyceride and so the transesterification process starts with three phases. Thus in most cases it is observed that for getting higher reaction rates and conversions, one needs higher temperature, pressure,

higher molar ratio of alcohol to triglycerides or other means to overcome mass transfer limitations (Di Serio *et al*., 2008). Use of co-solvent can improve the mass transfer limitation arising from phase difference. Cyclic ethers especially THF are preferred to use as co-solvent since they can dissolve both alcohol and the oil phase. The boiling point of THF is close to methanol making it easy to be removed and recovered along with excess methanol.

2.10.1 Calcium oxide catalyst

Calcium oxide (CaO) is a white crystalline basic solid having many industrial applications.It is mostly obtained from Calcium Hydroxide, waste materials amongst many other sources, the use of CaO as a heterogeneous catalyst has been in existence and has been reported in the transesterification of rapeseed oil (Peter and Thielman, 2008).

Table 2. 2: Properties of calcium oxide

Property	**Description**
Chemical name	Calcium Oxide
Chemical formula	CaO
Common name	Lime, Calx, quicklime, burnt lime
	Unslaked lime, fluxing lime, caustic lime
Density (g/cm^3)	3.40
Melting point (^0C)	2572
Boiling point (^0C)	2850
Heat of formation (Kcal/mol)	151.9
Heat of hydration (Kcal/mol)	15.1
Solubility of $Ca(OH)_2$ ($g/100g\ H_2O$)	0.219

Decomposition temperature (^{0}C)	547
Applications	In furnance lining, metal smelting, glass making, fertilizer, drying agent, mortar, paper and pulp production, drilling fluid,pollution control, water purification, sugar and cellulose industries, medical (destroys wart moles)

Source:Latimer and Hildebrand, (1951)

In making biodiesel production more sustainable, utilization of agro-based materials, waste materials and compounding heterogeneous catalysts is a matter of recent interest. Oyster and chicken egg shell have been evaluated as effective CaO catalysts in converting soybean oil to methyl esters. Nakatani *et al*., (2009) showed that using 25 wt.% of thermally activated Oyster shell (at 700 ^{0}C) with a 6:1 Methanol : oil molar ratio, gives a biodiesel product with over 70% yield and purity of 98.4wt.% in a 5hr reaction time at moderate 6:1 (MeOH : oil) ratio. Conversion was achievable at the expense of a higher catalyst and longer reaction time with 3 wt% of calcined egg shell at 1000 ^{0}C, (Wei, *et al.,* 2003). The authors found that the waste catalyst is capable of being reused up to three(3) times without much loss in activity.

The reaction of calcium carbide with water, producing acetylene and calcium hydroxide was discovered in 1862 and is shown in equation 2.3 below

$$CaC_2 + 2\ H_2O \rightarrow C_2H_2 + Ca(OH)_2 \qquad (2.3)$$

This reaction was the basis of the industrial manufacture of acetylene and is the major industrial use of calcium carbide. Equation 2.4 shows the formation of CaO from $Ca(OH)_2$When heated up to 512°C, the partial pressure of water in equilibrium with

Calcium hydroxide reaches 101kPa (normal atmospheric pressure) which decomposes Calcium hydroxide into Calcium oxide and water.

$$Ca(OH)_2 \rightarrow CaO + H_2O \qquad (2.4)$$

In the methanolysis of soybean oil, 15 wt. % CaO loaded ontomesoporous silica gave a 95.2% biodiesel yield at 5 wt.% catalystamount for a 8 hr reaction at 60 ◦C. In an attempt to transesterifythe lipid of the yellow green micro algae nano*Chloropsis oculata*. Umdu *et al*., 2009 used Al_2O_3 supported CaO and MgO as heterogeneous catalysts. They found that supported CaO and MgO showed far more activity than unsupported CaO and MgO.

2.10.2 Aluminium chloride catalyst

Anhydrous $AlCl_3$ has long been recognized as a strong Lewis acid in many organic reactions such as Friedel-Crafts reactions, Fries rearrangement, Scholl reaction, amongst others (Greenwood and Earnshaw, 1984).$AlCl_3$ catalysed transesterification of vegetable oil is far more effective than most catalysts due to its strong Lewis acid properties. It has also been demonstrated that $AlCl_3$ catalysis of stearic acid esterification suggests it as a potential alternative catalyst for biodiesel preparation using cheaper vegetable oil containing high amount of FFA**,** (Wang *et al.,* 2012). Anhydrous aluminium chloride is a powerful Lewis acid capable of forming Lewis acid-base adducts with even weak Lewis bases such as benzophenone and mesitylene. It forms tetrachloro aluminate $AlCl_4^-$ in the presence of chloride ions. Aluminum chloride is hygroscopic having a very pronounced affinity for water. It fumes in moist air and hisses when mixed with liquid water as Cl^- ions are displaced with H_2O molecules in the lattice to form the hexahydrate $AlCl_3 \cdot 6H_2O$ (also white to yellowish in colour). The anhydrous phase cannot be regained on heating as HCl is lost leaving aluminium hydroxide or alumina (aluminium oxide), the reactions are shown in equations 2.5 and 2.6 below.

$$Al(H_2O)_6Cl_3 \rightarrow Al(OH)_3 + 3\ HCl + 3\ H_2O \qquad (2.5)$$

On strong heating (~400°C), aluminium oxide is formed from the Aluminium hydroxide via:

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3\ H_2O \qquad (2.6)$$

2.11Optimization of Biodiesel Production

Response Surface Methodology (RSM) is an experimental strategy first described by Box and Wilson in 1951 for determining optimal conditions for multivariable systems and is considered an efficient technique for process optimization (Kong *et al*., 2004). RSM is useful in the solution of many types of industrial problems. Generally, one of these problems is optimization of responses in chemical processes. In the industrial world, a very important problem is determining conditions that optimize these processes.

RSM has been applied to optimize chemical reactions of sunflower oil transesterification with methanol in the presence of sodium hydroxide to produce the highest yield of bio-diesel. RSM addresses optimization via the following according to (Hill and Lewicki, 2006; Wan Omar and Saidina Amin, 2011):

(i) Providing an understanding of how test variables affect selected process response;

(ii)Determining interrelationships between test variables;

(iii) Characterizing combined effect of all influential test variables on process response

RSM has been increasingly used in bio-diesel production as a result of these factors. Ghadge and Raheman, 2006 for instance used this method to optimize pre-treatment process in reducing the FFA content of Mahua oil to less than 1% for maximum bio-diesel production. Findings include three variables ; methanol quantity, acid catalyst concentration and reaction time significantly affecting acid value of the product. Similarly, Tiwari *et al.*,(2007) deduced a quadratic polynomial model using RSM to optimize these same three parameters to reduce acid value of Jatropha oil (Jatropha curcas) before its conversion to bio-diesel.

2.12 Characterisation of Biodiesel

In relation to biodiesel analysis, several methods of analysis such as Gas chromatography (Meher *et al.*, 2006; Mittelbach, 1993; Knothe, 2001) and High Performance liquid chromatography have been used. Analysis of biodiesel is also accomplished by spectroscopic techniques, which can be done in combination with multivariate data analysis (Zhang, 2003; Knothe, 2001; Felizardo, 2006; Felizardo, 2007) Spectroscopic methods have been increasingly used to compliment and replace classic chemical methods. Infrared spectroscopy is one method that has had increased application due to its low cost, shorter time of analysis, non-destructiveness, and requirement of small quantities of sample, in addition to accuracy and reliability when associated with chemometrics. In some works, chemometrics was used for quantification of biodiesel blends using principal component regression (PCR), partial least square (PLS) and neural network (NN). (Oliveira*et al.,* 2007; (Bendini*et al.,* 2007;He*et al.,* 2007; Wang *et al.,* 2006)

CHAPTER THREE

3.0 Materials and Method

3.1 Preparation of Reagents

3.1.1 Preparation of potassium hydroxide (0.1 M) solution

Potassium hydroxide (56 g) , was dissolved with 20 cm^3distilled water in a 250 cm^3 beaker and transferred to a 1000 cm^3volumetric flask and made to the mark, to give a concentration of 1.0 M. Working solution of 0.1 M was prepared by diluting 100 cm^3 of stock solution to 1000 cm^3 mark in a volumetric flask.

3.1.2 Ethanolic potassium hydroxide (0.5 M) solution

Sodium hydroxide (56 g) was accurately weighed and dissolved to with 20cm^3 distilled water in a 250 cm^3 beaker. This was then transferred to a 1000 cm^3 volumetric flask and made to mark with dilute ethanol to give a concentration of 1.0 M. Working solution of 0.5 M was prepared by diluting 500 cm^3 of stock solution to 1000 cm^3 mark in a volumetric flask.

3.1.3 Hydrochloric acid (0.5 M) solution

Hydrochloric acid (83.3 cm^3), was diluted with 100 cm^3 distilled water in a beaker and made to 1000 cm^3 mark with distilled water in a volumetric flask to make 1.0 M concentration of stock solution. Working solution of 0.5M was prepared by diluting 41.6 cm^3 of stock solution in distilled water and made up to 1000 cm^3 mark with distilled water in a volumetric flask.

3.1.4 Potassium iodide KI (10% w/v) solution

Potassium iodide, (10g) was dissolved with 20 cm^3 distilled water in a beaker and was transferred to a volumetric flask and made to 100 cm^3 mark with distilled water to give 10 % w/v solution.

3.1.5 (5 %) nitric acidsolution

Nitric acid, (5 cm^3) was diluted with 10 cm^3 distilled water in a beaker and transferred to a 100cm^3 volumetric flask and made to mark with distilled water giving 5 % solution.

3.16(1 %) Starch indicator solution

starch powder (1g) was dissolved in 10cm^3 warm distilled water in a beaker volumetric flask and made up to 100 cm^3 with distilled water, 1 cm^3 of the solution was then transferred to a volumetric flask and made to 100 cm^3 mark with distilled water, giving 1% starch indictor solution

3.1.7 Sodium thiosulphate $Na_2S_2O_3$. $5H_2O$(0.1M) solution

Sodium thiosulphate, (24.82 g) was dissolved in 20 cm^3 distilled water in a beaker and transferred to a volumetric flask and made to 1000 cm^3 with distilled water giving 0.1 M solution.

3.18Preparation of sodium hydroxide (0.1 M) solution

Exactly 40 g of sodium hydroxide was dissolved to solution with distilled water and made to 1000 cm^3 mark to give 1.0 M concentration, working solution of 0.1 M was prepared by diluting 100 cm^3 of stock solution to 1000 cm^3 mark in a volumetric flask.

3.2 Methods

3.3 Sample Pretreatment

Waste cooking oil was warmed in a beaker on hot plate after which it was filtered under vaccum through cellulose filter paper to remove moisture due to the introduction of water from the fried foods into the oil. The filtration process also ensured the removal of solid materials in the oil sample. The oil sample was kept in a tightly covered plastic container and stored in a cool dark room. The collected carbide slurry was washed with distilled

water three times and allowed to settle before discarding the water. The sample was then dried in the oven to remove residual moisture.

3.4 Determination of Physicochemical properties

3.4.1 Acid value

Acid value was determined following ASTM method (ASTM – D 974(00). Oil sample (0.5g), was weighed into 250 cm^3 conical flask and 50 cm^3 of neutralized ethyl alcohol was added. The mixture was heated on a water bath to dissolve the sample. The solution was allowed to cool and titrated against 0.1M KOH using phenolphthalein as indicator, after which the acid value and free fatty acid was determined as follows:

$$Acid\ value\ = \frac{A\ X\ M\ \ 56.1}{w} \quad (3.1)$$

Where, A = cm^3 of 0.1M KOH consumed by sample

M = Molarity of KOH

W = weight in grams of the sample

$$\%\ FFA\ = \frac{A - B\ X\ M\ X\ 28.2}{W}$$

Where: A = cm^3 of 0.1M KOH consumed by sample

B= cm^3 of blank

M= molarity of KOH

W= weight in grams of oil sample

(3.2)

3.4.2 Saponification value of waste cooking oil

American Standard for Testing Material (ASTM) method- (D 5558-95) was used for the determination. The oil sample (2.0 g) was weighed into the conical flask and 25 cm^3 of 0.5M ethanolic solution of KOH was added and the resulting mixture was shaken for 20 minutes. This was subsequently titrated against 0.5M HCl with phenolphthalein as

indicator. The resulting end point was obtained when the pink colour changed into colourless. The same procedure was used for the blank titration without the oil or biodiesel sample. The Saponification value (SV) was then calculated using the expression;

$$Saponification\ value\ (S.V.) = \frac{56.1\ (B-S)\ X\ M\ \ of\ \ HCl}{weight\ of\ sample} \quad (3.3)$$

Where;

B – cm^3 of HCl required by blank

S – cm^3 of HCl required by sample

M- Molarity of HCl

3.4.3 Density

A 25 cm^3 density bottle with a FA2004N digital precision electronic analytical weighing balance was used for density determination at 15 °C according to ASTM D4052 method. The density bottle was first weighed empty, then with water in it and finally with the biodiesel sample. the density was then calculated as follows:

$$Density = \frac{W3-W1}{W2-W1} \quad (3.4)$$

where w_3 = weight of bottle with biodiesel sample

w_2= weight of sample with water

w_1= weight of empty density bottle

3.4.4 Viscosity

The viscosity was determined using kinematic viscosity recognizer item tool : KD R0515. A sample holder carried the sample and a calibrated thermometer was held in upright position and inserted into the bathat set temperature of 40 ^{0}C. The biodiesel was then allowed to freely flow and the time required for the meniscus to pass from the first to the

second timing mark was noted. The viscosity reading is noted and compared with ASTM standards.

3.4.5 Iodine value

The oil sample (0.5 g) was weighed into conical flask and 20 cm^3 of carbon tetrachloride was added to dissolve the oil. 25 cm^3 of prepared Wijj‟s Reagent was added in a fume chamber. The flask was then stoppered and the content was vigorously swirled. The flask was then placed in the dark for 35 minutes. At the end of this period, 20 cm^3 of 10% aqueous potassium iodide and 100 cm^3 of water were added. The content was titrated with 0.1M sodium thiosulphate solution. Few drops of 1% starch indicator were added and the titration continued by adding the sodium thiosulphate drop wise until coloration disappeared after vigorous shaking. The same procedure was used for the blank titration without the oil or biodiesel sample. The IodineValue is given by the expression:

$$Iodine\ Value\ (I.V) = \frac{12.69C\ (v1 - v2)}{M}$$

(3.5)

Where C = concentration of sodium thiosulphate

V1 = volume of sodium thiosulphate used for blank

V2 = volume of sodium thiosulphate used for determination

M = mass of sample

12.69 = Constant.

3.4.5 Sediment and water content

The sample of oil 50 cm^3 was placed in a test tube and its content was stoppered and allowed to attain the laboratory temperature. The tube was placed in a trunnion cup opposite another filled tube to establish a balanced condition of the mechanical shaker. The samples were agitated at a speed of 1800 rpm for 10 minutes to ensure homogeneity. The

oil was then separated from the fractions and weighed. The combined water and sediment at the bottom of the tube was the reported as percentage of sample. (ASTM D2709 – 96).

$$Moisture\ and\ Sediment = \frac{(w1 - w2)}{w1} X\ 100$$

W_1= Initial weight of oil

W_2= Final weight of oil

3.5 Fatty Acid Methyl Ester (FAME) Profile

The profile of fatty acids present in the oil and biodiesel samples was analyzed using GC-MS. This is a combination of two techniques used for analyzing mixtures of components; The gas chromatography separates the components in the mixture using the principle explained while the mass spectroscopy characterizes each of the components individually. As the individual compounds elute from the GC column, they enter the electron ionization detector in the mass spectroscopy, from where they are bombarded with a stream of electrons causing them to break apart into fragments. The analysis was carried out using a GC PERICHROM PR2100 equipped with a capillary column (50 m × 0.201 mm × 0.50 _m) with HP-PONA stationary phase and flame ionization detector. The carrier gas was helium at a flow rate of 0.6 ml/min. The GC column was kept at 120 ◦C for 5 min, heated at a rate of 4 ◦C/min up to 225 ◦C and kept at 225 ◦C for 20 min. The injector and detector temperatures were set at 250 ◦C. External standard method was used for GC calibration. Standard solutions of methyl esters were prepared and injected into the GC under identical conditions. Then, calibration curve for each methyl ester was derived and used for quantification of methyl esters concentration in the samples. The preparation of the purified biodiesel samples for injection into the GC was carried out as follow: 0.3 g of the biodiesel sample was dissolved in 5 ml of *n*-hexane and 1 µL of this solution was injected into theGC machine.

3.6 Determination of Functional groups

To investigate the position and presence of characteristic organic functional groups, FTIR analysis was carried out using KBr. The FTIR spectra were recorded on a Shimatzu Fourier Transform Infrared Spectrometer (FTIR). The sample was mixed with Potassium bromide (KBr) and then smeared to give a small transparent disc of 13 mm diameter. A background spectrum of pure KBr was run before that of the spectrum of any sample to account for any absorption due to impurities in the KBr. The disc containing the sample was then placed in the infrared spectrometer and the spectrum of the samples were collected. A total of twenty (20) scans were collected for each measurement over the spectral range of 4000-400 cm^{-1} with a resolution of 4 cm^{-1}. All spectra were presented without baseline correction or normalization. With this technique, vibrational excitation of bonds as a result of interaction between certain wavelength of infrared radiation and molecules of the catalysts are observed depending on the functional group of the compound. The types of bond excitation that can occur are stretching (higher energy) and bending (lower energy) vibrations.

3.7 Pretreatment and Preparation of Alkali Supported on Calcium Oxide (NaOH/CaO) Catalyst

The waste carbide slurry was washed three times with distilled water after which it was heated in a murfle furnace at 700 ^0C for three hours after which it was cooled in a desiccator over silica gel. The catalyst was prepared by incipient wetness impregnation of CaO powder with an aqueous solution of NaOH. A known weight of the prepared calcium oxide (60 g) was measured into a beaker and impregnated with 50 cm^3 0.1 M sodium hydroxide (50 wt. %) solution. The mixture was stirred for one hour to homogenize after

which the impregnate (NaOH/CaO) was dried in oven at 100°C overnight and further dried in a desiccators over silica gel**. (**Kang, 2005**)**

3.8.1 Determination of Calcium Content of Calcined Carbide Slurrry

The total calcium content of the prepared CaO was determined after calcinations at high temperatures using Atomic absorption spectroscopy (AAS). The sample (0.01 g) was dissolved in 5 cm^3 of 5% HNO_3 solution and made up to 100 cm^3 mark distilled water. This was then taken for AAS analysis.

3.8.2 Determination of functional groups on prepared calcium oxide (CaO)

The presence or absence of some functional groups like carbonates (CO_3^{2-}) could affect the purity of the catalyst. FTIR Analysis was carried out using KBr. The FTIR spectra were recorded on a Shimatzu Fourier Transform Infrared Spectrometer (FTIR) .The sample was mixed with Potassium bromide (KBr) and then ground to a homogeneous blend and compressed to give a small transparent disc of 13 mm diameter. The analysis was then carried out as in section 3.6.

3.8.3Determination of size and morphology of carbide slurry and calcium oxide

To determine the size and surface morphology of the samples, before and after calcination, Scanning Electron Microscopy (SEM) was carried out using a Phenon™X-pro Scanner.Minimal preparation includes the acquisition of the sample and placing it on a Clean Carbon strap that will be attached on the sample holder, which fit into the SEM chamber, and some accommodation to prevent charge build-up and also prevent the sample from making contact with the Detector.

3.9 Optimization of Esterification of Waste Cooking Oil (WCO)

In order to reduce the free fatty acid content of the waste cooking oil, the esterification reaction was optimized using a two level, thee factorial design (2^3) provided by the software Design Expert 7.0.which was employedto design the experiments and fit a quadratic response surface to experimental data; This gave rise to eight experiments. Selection ofthe factors was based on the fact that for a given waste cooking oil (i.e. for waste cooking oil with certain properties such asfree fatty acid and moisture content), parameters includingreaction temperature, molar ratio of methanol to oil, catalystconcentration, reaction time and catalyst type are the influencing factors affecting esterification reaction, (Dias *et al.*, 2011). The design of experiments is shown in Table 3.1. and was used for all the esterification experiments.

Table 3. 1: Experimental Design of Process Parameters (factors)

Run	Alcohol:oil Molar ratio	Catalyst (wt%)	Time (hr)
1	4.00	2.00	2.30
2	4.00	5.00	1.00
3	4.00	2.00	1.00
4	4.00	5.00	2.30
5	6.00	2.00	2.30
6	6.00	5.00	2.30
7	6.00	5.00	1.00
8	6.00	2.00	1.00

3.9.1 Esterification using 0.5 M sulphuric acid catalyst

100 g of the oil sample was charged into the flask and warmed for 20 minutes while stirring till temperature was at 65^0C. A measured volume of the catalyst and methanol was then added to the flask depending on the combination of factors in the experimental run been

carried out as prescribed in Table 3.1, while reaction mixture was stirred vigorously at constant stirring rate for all experiments. After the designated time for the reaction has been reached, the flask was removed from the hot plate and the reaction was stopped by quickly submerging the flask in a water bath to cool the mixture to room temperature. The reaction mixture was then transferred to a separatory funnel to allow separation of products and left to settle overnight. When the mixture became biphasic, the upper and the lower layers were isolated by tapping off the lower layer. The upper layer, which mainly comprised of methyl ester, was later washed with distilled water to remove any impurities before heating in the oven at 105 ^{0}C for 8 hr to remove traces of water and unreacted methanol.

3.9.1 Esterification using aluminum chloride catalyst

100 g of the oil sample was charged into the flask and warmed for 20 minutes while stirring till the temperature reached at 65^{0}C. A measured weight of the catalyst and methanol is then added to the flask depending on the combination of factors in the experimental run been carried out, while reaction mixture was stirred vigorously at constant stirring rate for all experiments. After the designated time for the reaction has been reached, the flask was removed from the hot plate and the reaction was stopped by quickly submerging the flask in a water bath to cool the mixture to room temperature. The reaction mixture was then transferred to a separatory funnel to allow separation of products and left to settle overnight. When the mixture became biphasic, the upper and the lower layers were isolated by tapping off the lower layer. The upper layer, which mainly comprised of methyl ester, was later washed with distilled water to remove any impurities before heating in the oven at 105 ^{0}C for 8 hr to remove traces of water and unreacted methanol.

3.10 Transesterification of Esterified Waste Cooking Oil (WCO)

Transesterification was done to convert the free fatty acids in the esterified waste cooking oil to esters using methanol and catalyst. The produced esters are known as fatty acid

methyl esters (FAME). Transesterification was carried out using alkali, aluminium chloride and alkali supported calcium oxide catalysts.

A measured weight ofesterified oil (100 g) wasadded into the reactor and warmed to 60 ^{o}C then the catalyst (5 wt %) to the oildissolved in methanol in the ratio (6:1) wasgently charged into the reactor while stirring, the mixture was stirred continuously at 600rpm to avoid the mass transfer limitationsand a magnetic bar was used for stirring while maintaining the temperature between 60-65 ^{o}C for 2 hours, after which heating and stirring were stopped and the reactor was removed from condenser and heater.

The reaction mixture was transferred into a separation funnel and left for 8 hours undisturbed to allow separation of glycerol from the fatty acid methyl ester phase. The lower glycerol phase was then tapped off anda rotary evaporator was used to remove excess methanol. After separation, the crude biodiesel was washed 3-4 times with warm distilled water to remove trace amounts of catalyst and glycerol in the methyl ester. The washed biodiesel was then dried at 100 ^{0}C in the oven and weighed. All experiments were repeated twice and the best yield was then recorded. The percentage yield of biodiesel fatty acid methyl esters (FAME) was calculated as:

$$Yield = \frac{Weight\ of\ biodiesel\ yield}{Theoretical\ weight\ of\ biodiesel\ yield} \quad X\ 100$$

(3.6)

3.11 Determination of Physicochemical and Fuel Properties of Biodiesel

All physicochemical properties were carried out as in the methods stated in section 3.4. The determined Fuel properties include:

3.11.1 Cetane number

The cetane number was determined using automatic cetane analyzer tool; KD R3034, the biodiesel sample (50 cm^3) was placed in the inner sample holder and inserted into the outer sample holder, at room temperature. The machine gives the cetane reading of the sample.

3.11.2 Cloud point and Pour point

The cloud and pour points were determined using the Haeckel Caton Changsha cloud and pour point analyzer tool; KD R1072. For cloud point, sample was placed in the sample holder fitted with a thermometer. As the machine is set on the temperature begins to drop. The temperature at which the first crystal is formed was noted as the cloud point. For the pour point, the temperature of the machine starts to increase and the temperature at which the sample cannot move is noted as the pour point. 50 cm^3 of sample was used in both cases.All results were compared to ASTM standards.

3.11.3 Flash point

The Haeckel Cation Changsha automatic flash point tester; KD R0211 was used in determining the point of ignition of the various biodiesel samples. The sample is placed in a sample holder and the ignitor connected to a gas supply is placed on top the sample holder containing the sample, as the machine is set on and gas is supplied temperature begins to read and the temperature at which the sample flames up is recorded as the flash point.

3.12Fatty Acid Profile

The profile of corresponding esters of fatty acids also known as fatty acid methyl esters (FAME) in prepared biodiesel was analyzed using gas chromatographic – mass spectrophotometer as in section 3.5.

3.13Determination of Functional groups

The major functional groups peculiar to biodiesel samples were determined in the prepared biodiesel samples. The analysis was carried out as in section 3.6.

3.14 Reusability of NaOH/CaO Catalyst

To investigate the reusability of the prepared alkali supported on calcium oxide (NaOH/CaO) catalyst, the transesterification reactions were carried out three more times with the same esterified oil weight (100g), catalyst weight (5 wt%), reaction time and temperature set at 2.30 hr and 65 ^{0}C for all the tranesterification experiments. After the reaction cycle the spent catalyst wasseparated from reaction mixture by centrifugation and washed with methanol to remove adsorbed residual methyl ester and water formed in the previous reaction cycle. Washed catalyst was used in next transesterification reaction cycles this was repeated for all three experiments and biodiesel yield was calculated.

3.15 Statistical Analysis

Experimental designwas generated using Design Expert 7.0. The statistical software was used in analysis via Response surface methodology(RSM) in order to fit the polynomial order equation. The response free fatty acid (FFA) percent reductionwere initially fitted to the factors via multiple regressions. The quality of the fit was determined using the coefficient of determination (r^2) and analysis of variance (ANOVA). The sum of squares for main and interaction effects was also calculated. The significant factors (main and interaction) were identified by ANOVA technique (Aigbodion *et al.*, 2010) and the quadratic response surface model is fitted to the Equation(Zang *et al.*, 2009). In this experiment the response surface plot was the focus to determine the influence of factors interaction on esterifcation of waste cooking oil with the aim of reducing the free fatty acid content.

CHAPTER FOUR

4.0 RESULTS

4.1 Physicochemical Analysis, Gas Chromatography-Mass Spectrometry and Fourier Transformed Infrared Spectroscopy for Waste Cooking Oil

The result of the physicochemical properties of waste cooking oil indicated the oil had high amount of moisture and sediment content. Acid value and viscosity were also found to be high as presented in Table 4.1 Hence the waste cooking oil would require pretreatment before transesterification into biodiesel.

Table 4.2 shows the fatty acid profile of the waste cooking oil, from where palmitic, myristic, stearic, oleic and linoleic acids were identified as the major fatty acids. The percentages of the fatty acids indicated that the waste cooking oil to contain more of sataurated fatty acids and long chain fatty acids.

The fourier transformed infrared (FTIR) spectra of waste cooking oil is shown in Figure 4.1 and indicated the presence of free fatty acids and moisture at the 1737 cm $^{-1}$and 3446.91 cm^{-1} bands.

4.2 Properties of Carbide Slurry and NaOH/CaO Catalyst

4.2.1 Functional group analysis of carbide slurry and NaOH/CaO catalyst

Figure 4.2 – 4.3 shows the fourier transformed infrared (FTIR) spectra of carbide slurry and prepared calcium oxide catalyst. It confirms the initial presence of the carbonate group in the carbide slurry and its absence in the calcium oxide catalyst.

4.2.1 Scanning electron microscope (SEM)

The scanning electron microscope (SEM) micrograph of waste carbide slurry and prepared calcium oxide catalyst is shown in Plate 4.1-4.2. An improved surface area was observed in the prepared catalyst following the tiny crystal fragments obtained as to the bulky crystals in the slurry.

Table 4. 1: Physicochemical properties of waste cooking oil

Property	Unit	Value
Density	g/cm^3	0.89 ± 0.07
Acid value	mgKOH/g	3.80 ± 0.74
Free fatty acid	%	1.90 ± 0.21
Viscosity	mm^2/s	18.60 ± 0.36
Moisture and sediment	%	3.60 ± 0.22
Iodine value	g iodine/g	112.5 ± 0.54
Saponification value	mgKOH/g	248.1 ± 0.37

Table 4. 2: Fatty acid profile of waste cooking oil

Methyl Ester	Percentage composition
Palmitic acid methyl ester (C16:0)	42.50
Myristic acid methyl acid ester (C14:0)	0.86
Stearic acid methyl ester (C18:0)	9.00
Oleic acid methyl ester (C18:1)	39.85
Linoleic acid methyl ester (18:2)	2.10

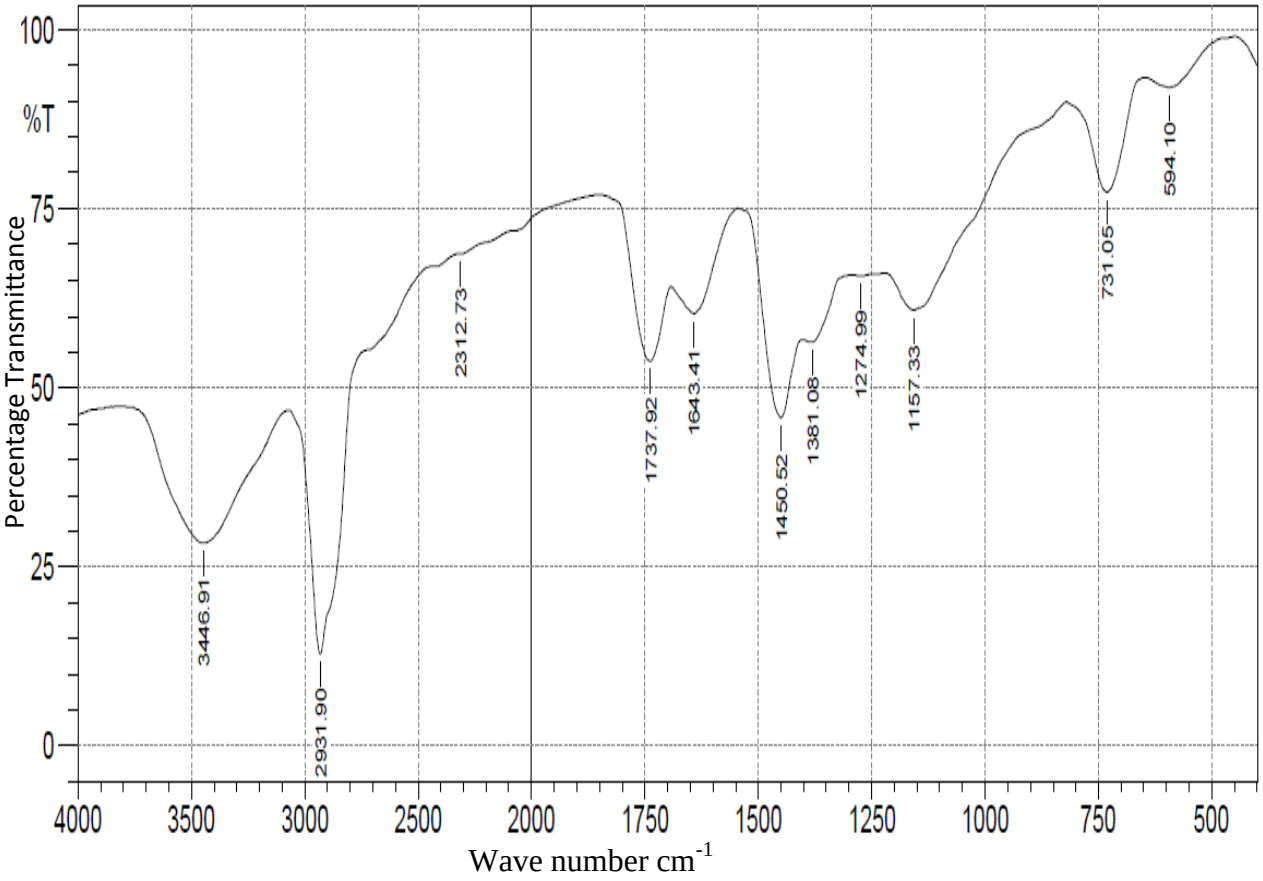


Figure 4. 1: Fourier transformed infrared spectra of waste cooking oil

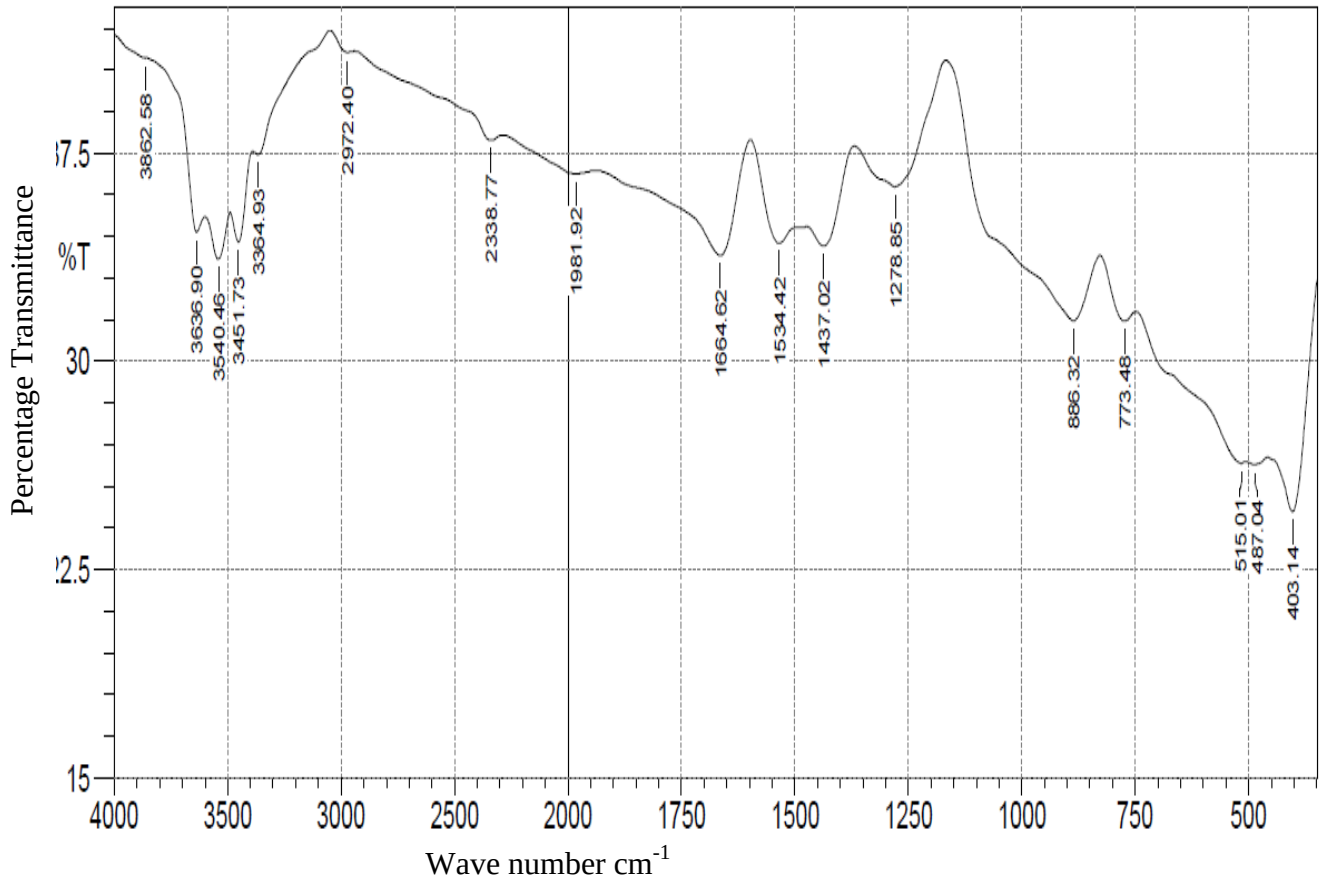


Figure 4. 2: Fourier Transformed Infrared Spectra for Waste Carbide Slurry

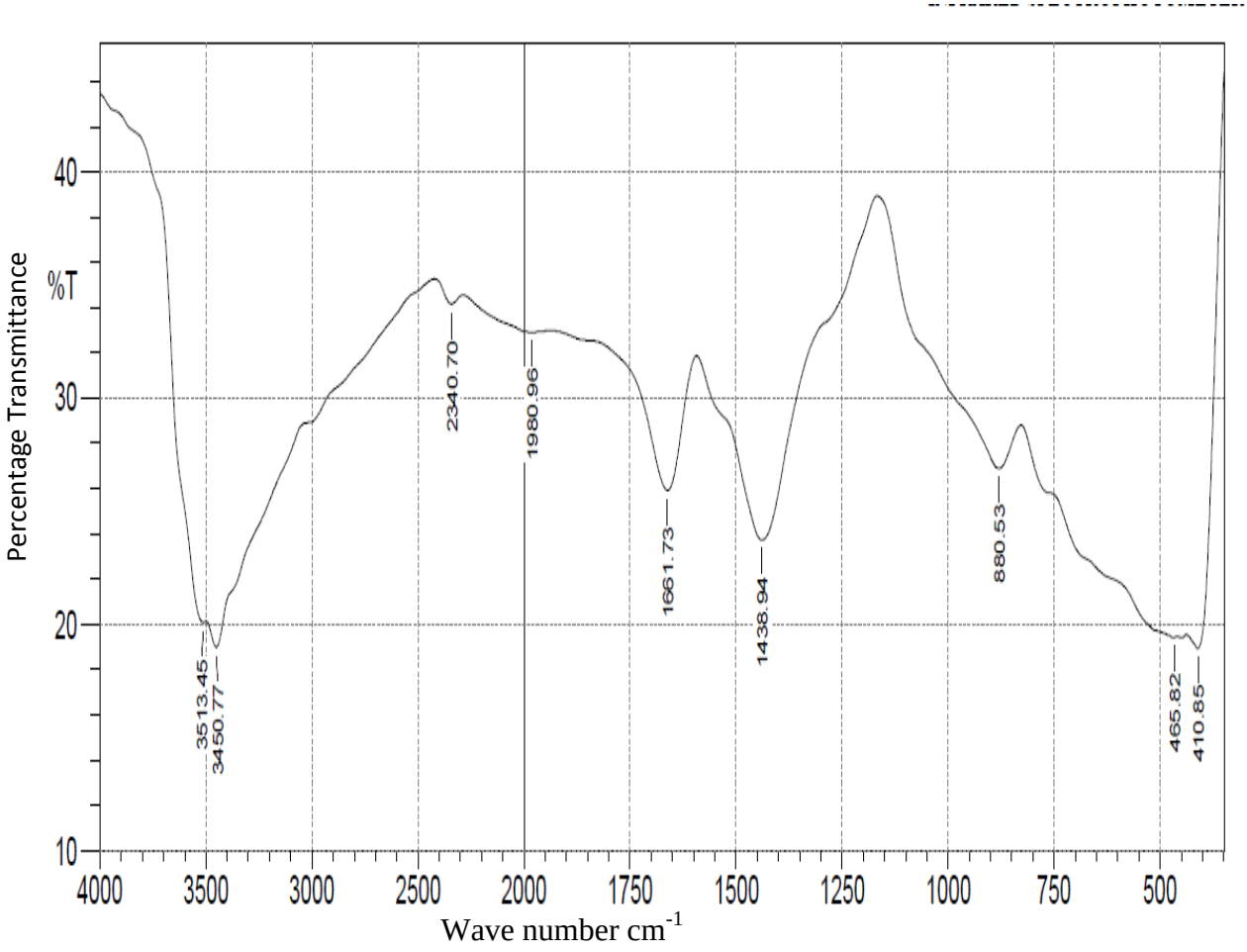


Figure 4. 3: Fourier Transformed Infrared Spectra for Prepared Calcium oxide

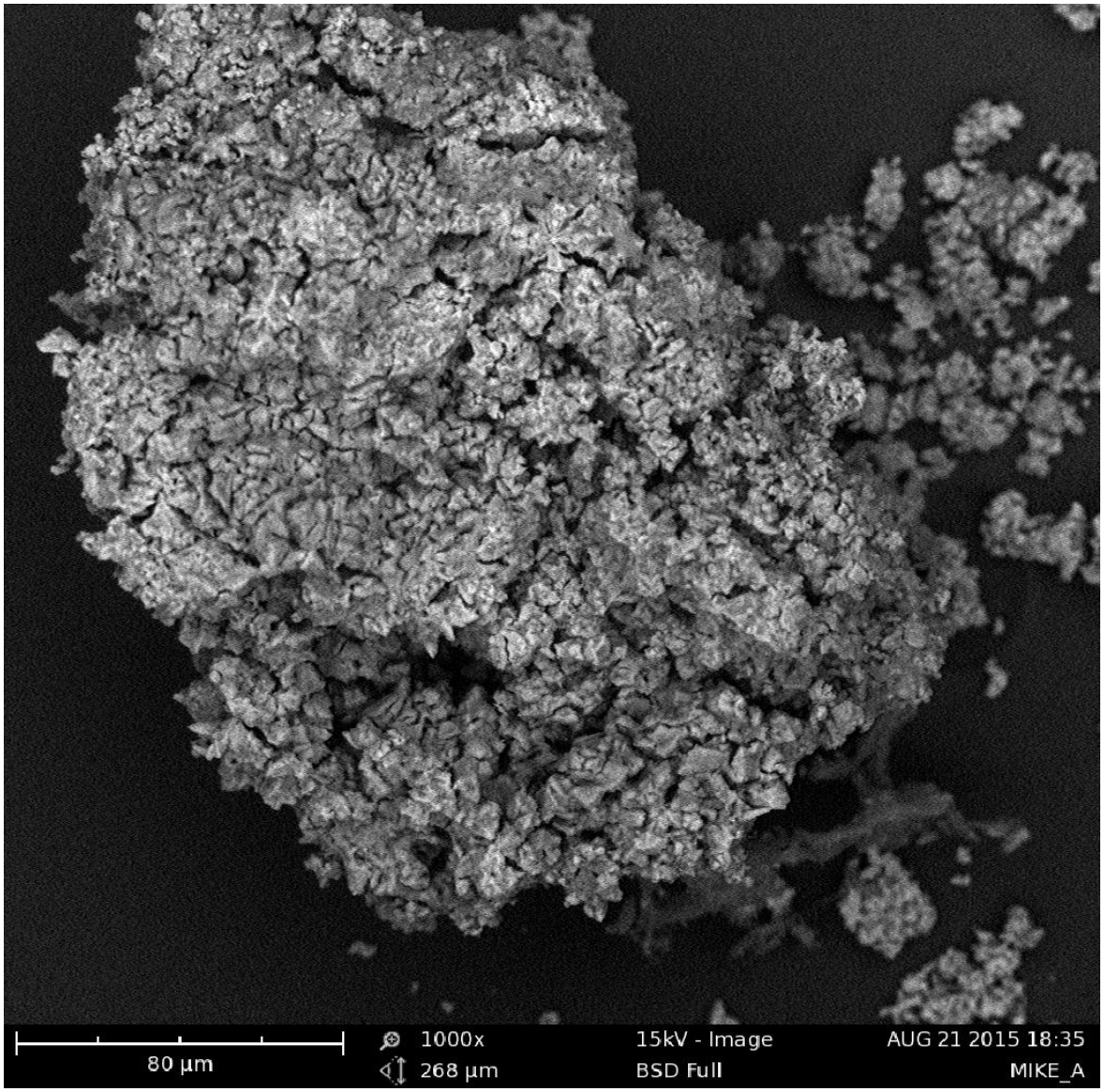


Plate 4. 1: Scanning Electron Micrograph of waste carbide slurry

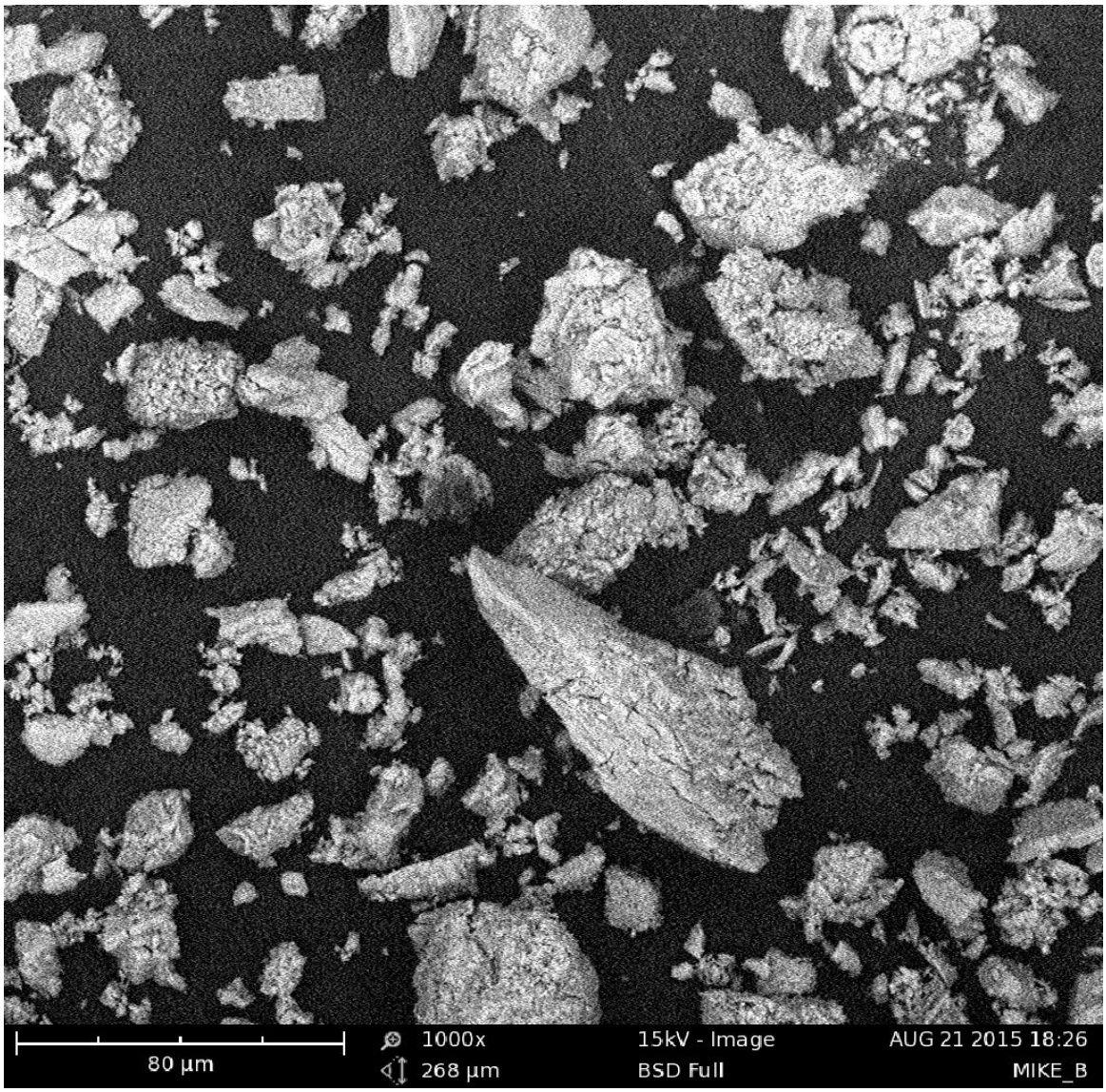


Plate 4. 2Scanning Electron Micrograph of Modified Calcium Oxide Catalyst

4.3 Optimization of Esterification of Waste Cooking Oil

4.3.1 Experimental design, response surface plot and main effects for sulphuric acidesterification of waste cooking oil

The results of the experimental design for interaction of process parameters (factors) used in H_2SO_4 esterification of waste cooking oil is presented in Table 4.3. A two level three factorial design giving eight (8) runs was used and the response was the percentage free fatty acid (FFA) reduction.

Table 4.4 shows the main effect of the experimental factors both individually and combined in the H_2SO_4 esterification of waste cooking oil.

The interaction of experimental factors was presented as response surface plots shown in Figures 4.4 – 4.6. The response plot for factor interaction between time (hr) and catalyst weight against % FFA reduction is shown in Figure 4.4 while the response surface plot for factor interaction between catalyst (wt %) and molar ratio against percentage free fatty acid conversion is shown in Figure 4.5. The interaction shown in Figure 4.6 indicates response surface interaction for time and molar ratio.

Table 4. 3: Experimental Design with responses for H_2SO_4 catalyzed esterification of Waste Cooking Oil

Run	Molar ratio	Catalyst (wt%)	Time (hr)	FFA Reduction (%)
1	4.00	2.00	2.30	74
2	4.00	5.00	1.00	81
3	4.00	2.00	1.00	79
4	4.00	5.00	2.30	88
5	6.00	2.00	2.30	91
6	6.00	5.00	2.30	83
7	6.00	5.00	1.00	76
8	6.00	2.00	1.00	79

Table 4. 4: Main effect of factor interaction in H_2SO_4 catalyzed esterification of Waste Cooking oil

Term	Effect	Sum square	% Contribution
A-Molar ratio	0.2313	0.1070	15.09
B-Catalyst	-0.0461	0.0043	0.618
C-Time	-0.2372	0.1125	15.87
AB	0.0408	0.0033	0.471
AC	0.0727	0.0105	1.492
BC	-0.4276	0.3657	51.59
ABC	-0.2294	0.1053	14.86
ANOVA	P value = 0.034	F value= 42.3	R_2 = 0.8796

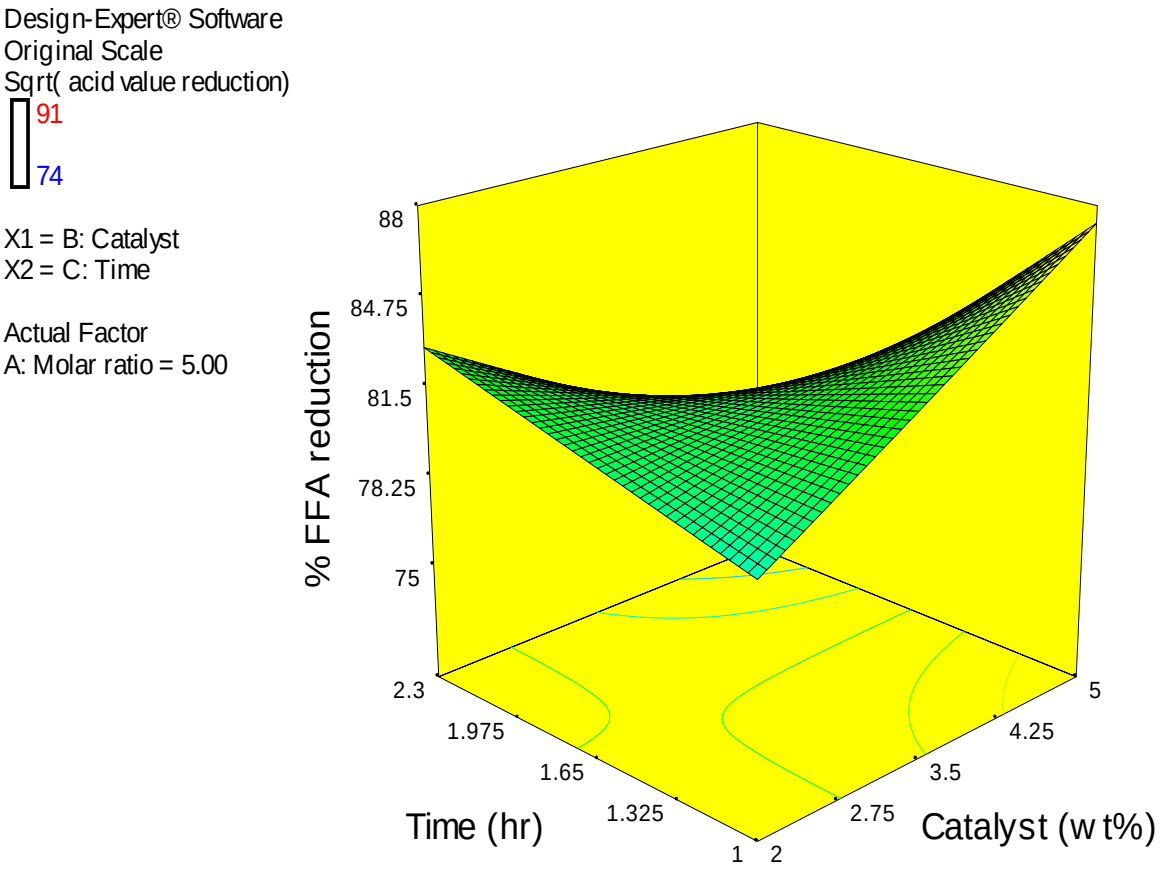


Figure 4. 4: Response surface plot for factor interaction between time and catalyst against % FFA conversion

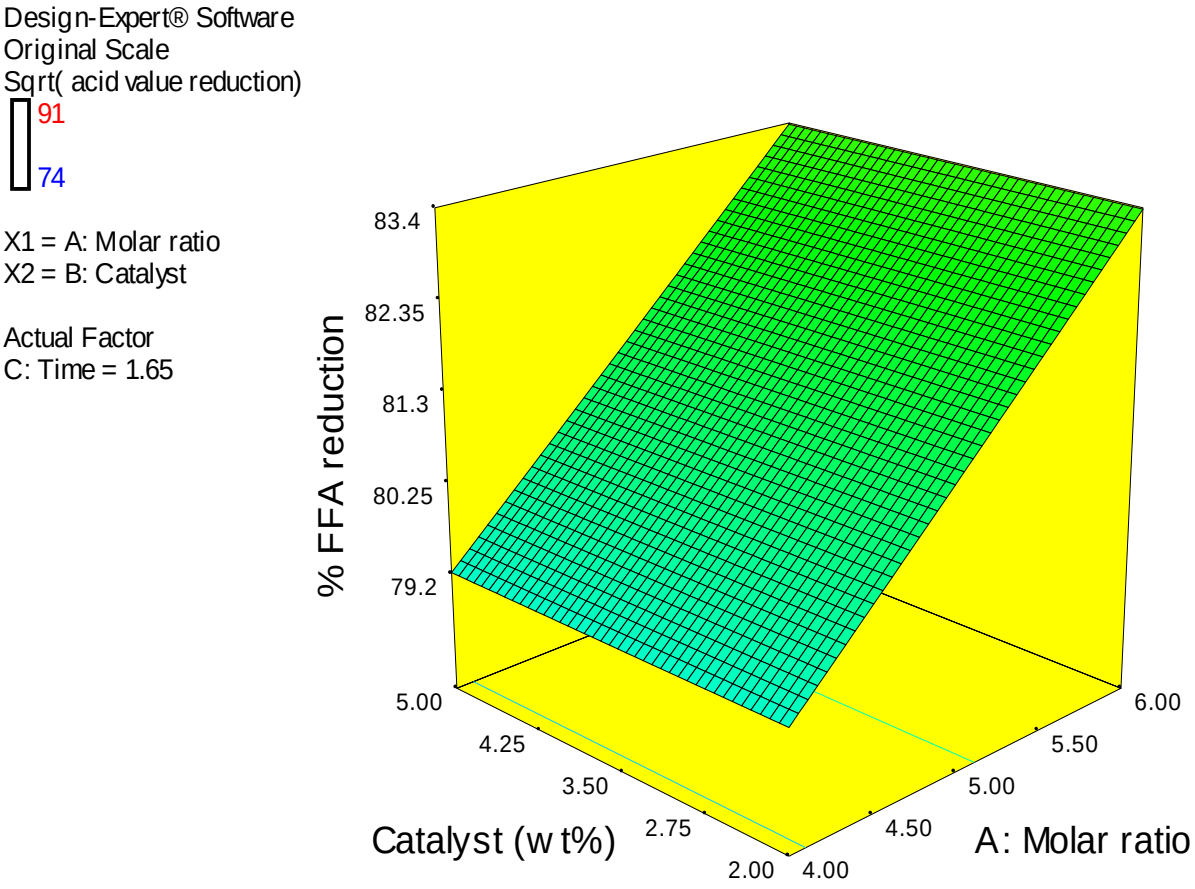


Figure 4. 5: Response surface plot for factor interaction between catalyst and molar ratio against % FFA conversion

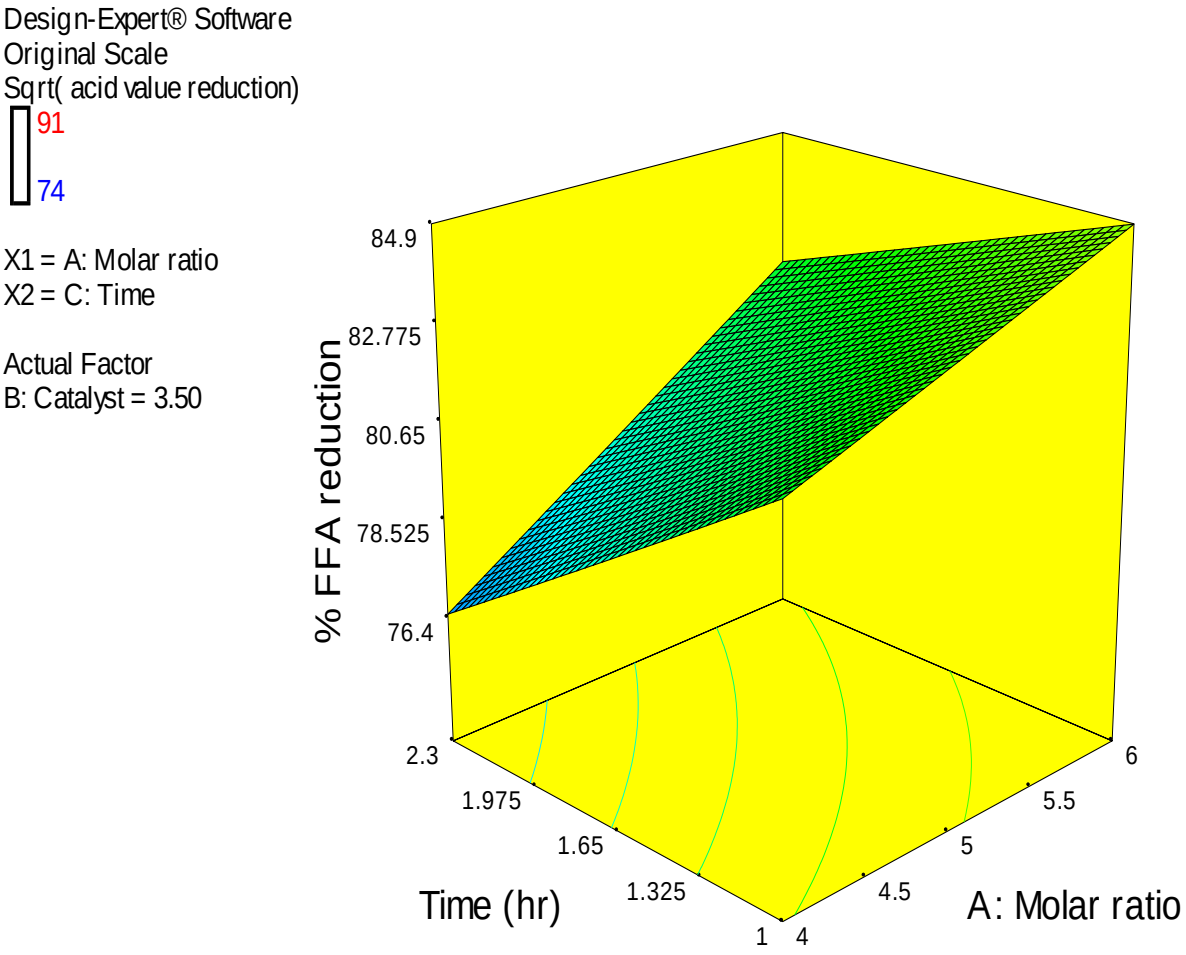


Figure 4. 6: Response surface plot for factor interaction between time and molar ratio against % FFA conversion

4.3.2 Experimental design, response surface plot and main effects for aluminium chloride esterification of waste cooking oil

The results for interaction of process parameters (factors) used in aluminium chlorideesterification of waste cooking oil is presented in Table 4.5. A two level three factorial design giving eight (8) runs was used and the response was the percentage free fatty acid (FFA) reduction.

Table 4.6 shows the main effect of the experimental factors both individually and combined in the aluminium chlorideesterification of waste cooking oil.

The interaction of experimental factors was presented as response surface plots shown in Figures 4.7 – 4.9 The response plot for interaction of factors between time (hr) and molar ratio against percentage free fatty acid conversion is shown in Figure 4.7 while that for the interaction of factors between time (hr) and catalyst (wt %) against % FFA conversion is shown in Figure 4.8. The response surface plot for interaction of factors between catalyst (wt %) and molar ratio against percentage free fatty acid conversion is shown in Figure 4.9.

Table 4. 5: Experimental Design with responses for $AlCl_3$ catalyzed esterification of Waste Cooking Oil

Run	Molar ratio	Catalyst (wt%)	Time (hr)	FFA Reduction (%)
1	4.00	2.00	2.30	67
2	4.00	5.00	1.00	71
3	4.00	2.00	1.00	83
4	4.00	5.00	2.30	87
5	6.00	2.00	2.30	71
6	6.00	5.00	2.30	79
7	6.00	5.00	1.00	94
8	6.00	2.00	1.00	70

Table 4. 6: Main effect of factor interaction in $AlCl_3$ catalyzed esterification of Waste Cooking oil

Term	Effect	Sum square	% Contribution
A-Molar ratio	6.750	91.125	12.485
B-Catalyst	-9.750	190.125	26.049
C-Time	8.250	136.125	18.6505
AB	-1.250	3.1250	0.42816
AC	7.750	120.125	16.4583
BC	4.250	36.125	4.94948
ABC	8.750	153.125	20.9796
ANOVA	P value = 0.014	F value= 45.1	R_2 = 0.9103

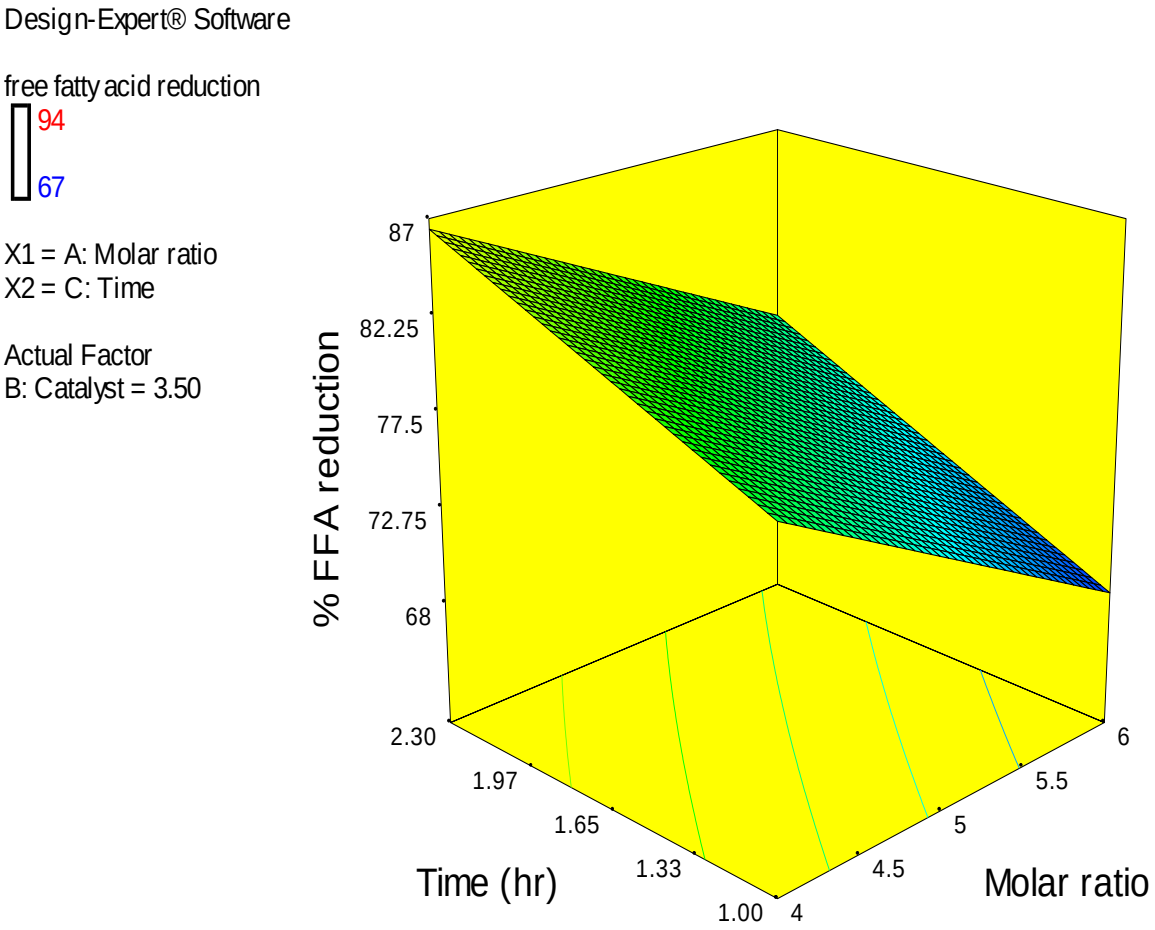


Figure 4. 7: Response surface plot for factor interaction between time and molar ratio against % FFA conversion

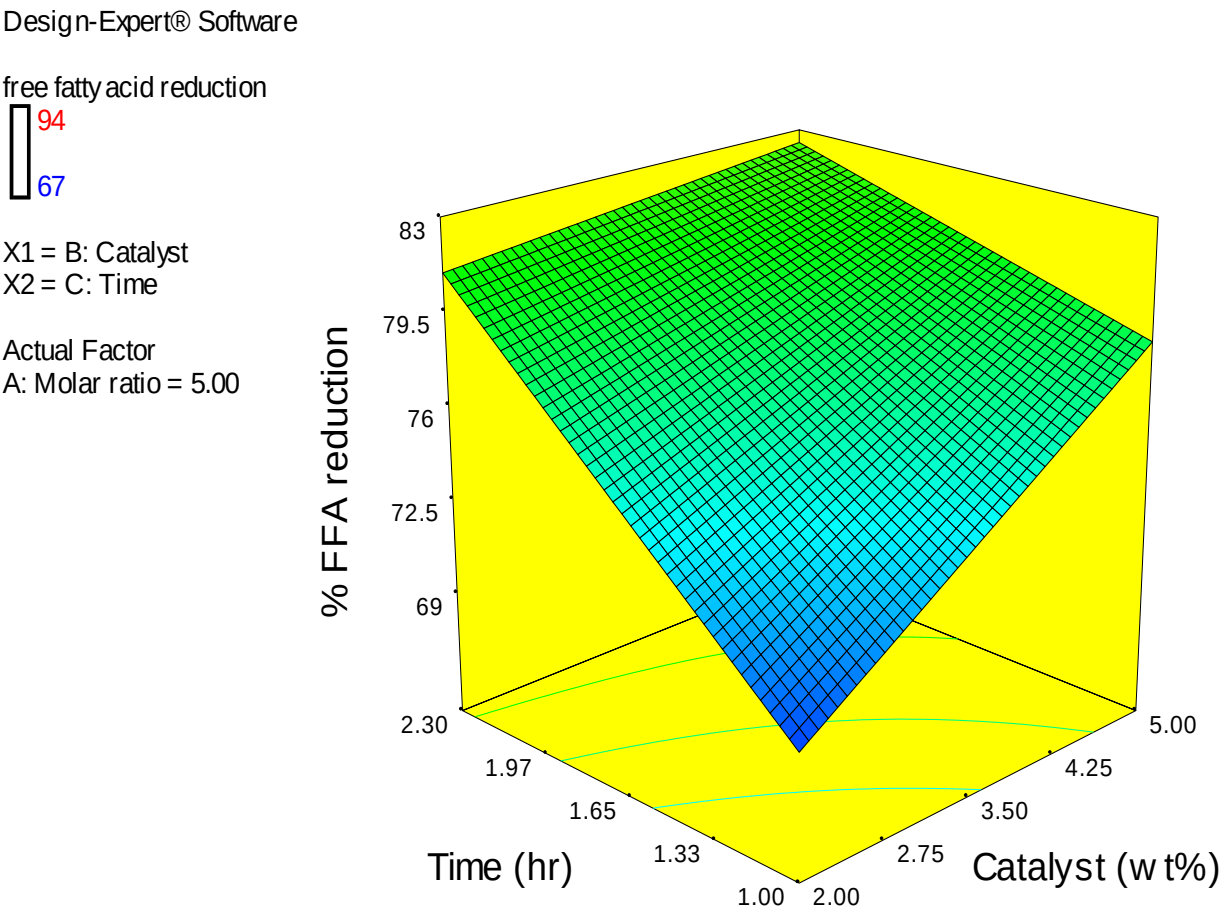


Figure 4. 8: Response surface plot for factor interaction between time and catalyst amount against % FFA Conversion

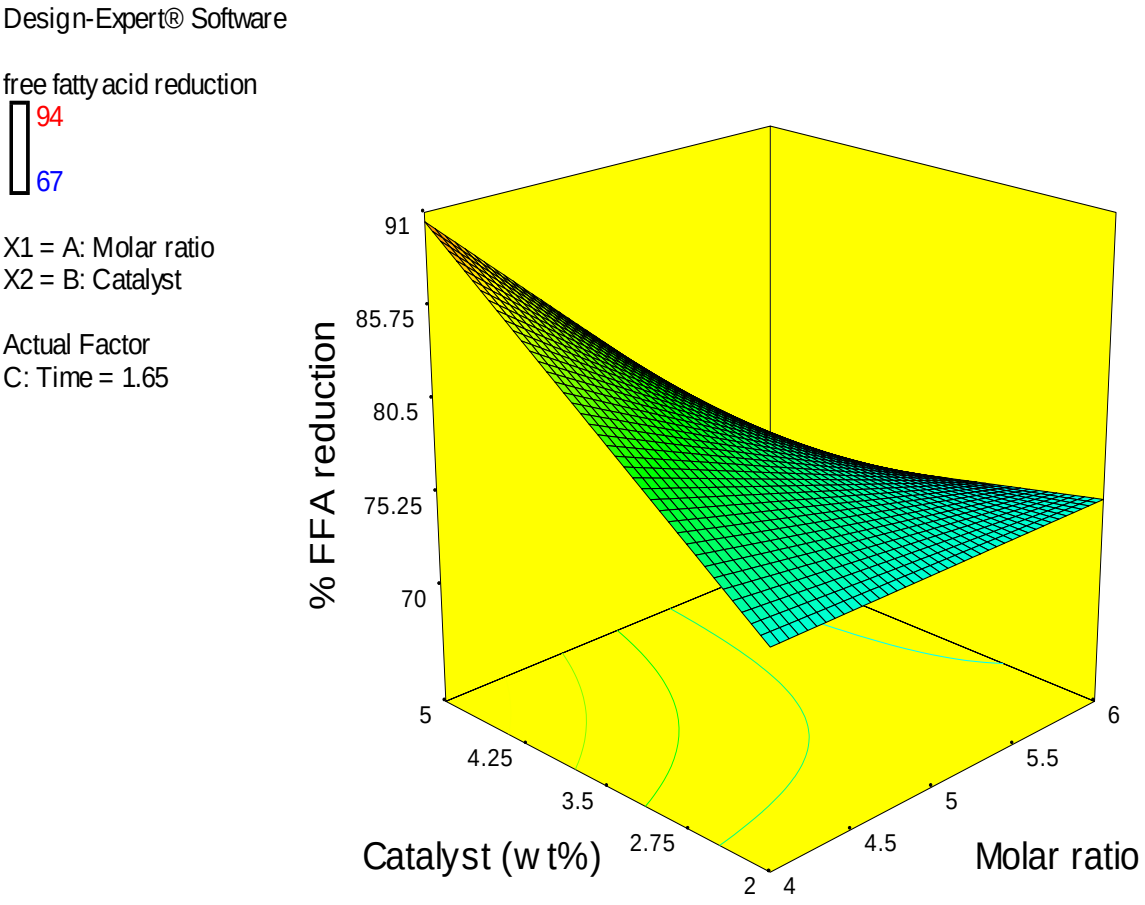


Figure 4. 9: Response surface plot for factor interaction between catalyst and molar ratio against %FFA Conversion

4.4Physicochemical Properties, Gas Chromatography and Fourier Transformed Infrared Spectroscopy of fatty acid methyl esters (FAME)

Transesterification was carried out on the esterified oil using $AlCl_3$, NaOH and NaOH/CaO catalysts. The results of the physicochemical properties are presented in Table 4.7 A reduction in the acid value, moisture and sediment content and viscosity suggests that transesterification occurred.

The profile of fatty acid methyl ester composition of the biodiesel samples is shown in Table 4.8. Similar fatty acids observed in the waste cooking oil.

Fourier transformed infrared spectroscopy (FTIR) spectra of fatty acid methyl ester (FAME) samples are presented in Figures 4.10 – 4.12 for $AlCl_3$, NaOH, and NaOH/CaO FAME samples. The presence of ester carbonyl peak at 1700 cm^{-1} and of alkyl group at 2900 cm^{-1}suggests a stripping off of glycerol and formation of ester.

The result for reusability of NaOH/CaO catalyst are presented in figure 4.13. It shows a slight improvement on the fourth use due to regeneration.

Table 4. 7: Physicochemical properties of $AlCl_3$, NaOH and NaOH/CaO catalyzed biodiesel samples

Property	**Unit**	**NaOH**	**$AlCl_3$**	**NaOH/CaO**	**ASTM Std.**
Density 15^0C	g/cm^3	0.86 ± 0.31	0.88 ± 0.28	0.86 ± 0.35	0.86-0.90
Acid value	(mgKOH/g)	0.26 ± 0.10	0.12 ± 0.21	0.18 ± 0.24	Max 0.50
FFA	%	0.13 ± 0.11	0.06 ± 0.20	0.09 ± 0.24	< 1%
Cloud point	(^0C)	11.0 ± 0.62	10.0 ± 0.53	12.0 ± 0.49	-3 to 12
Pour point	(^0C)	6.0 ± 0.25	6.0 ± 0.36	7.0 ± 0.47	-15 to 16
Viscosity 40^0C	(mm^2/s)	4.1 ± 0.73	2.9 ± 0.19	4.2 ± 0.13	1.9 – 6.0
Flash point	(^0C)	167 ± 0.51	158 ± 0.42	164 ± 0.51	Min 130
Cetane number	(^0C)	61 ± 0.33	56 ± 0.58	64 ± 0.27	Min 47
Iodine value	(iodine/g)	119.60 ± 0.52	103.34 ± 0.71	124.21 ± 0.64	Max 120
Saponification value	(mgKOH/g)	197.08 ± 0.48	205.29 ± 0.35	190.66 ± 0.44	
Moisture and sediment	(%)	<0.05	<0.05	<0.05	Max 0.05
PercentageYield of Biodiesel for:		**89.7 ± 0.16**	**90.2 ± 0.57**	**92.22 ± 0.31**	

Table 4. 8: Fatty acid Methyl ester (FAME) profile and percentage yield of biodiesel samples with

Methyl ester	**NaOH**	**$AlCl_3$**	**NaOH/CaO**
Palmitic acid methyl ester (C16:0)	31.66	24.61	1.08
Myristic acid methyl ester(C14:0)	1.52	8.60	35.90
Stearic acid methyl ester(C18:0)	7.96	9.31	6.35
Oleic acid methyl ester(C18:1)	34.35	30.26	46.30
Linoleic acid methyl ester(C18:2)	9.27	11.14	7.94
% Yield of biodiesel for:	**89.7**	**92.20**	**92.22**

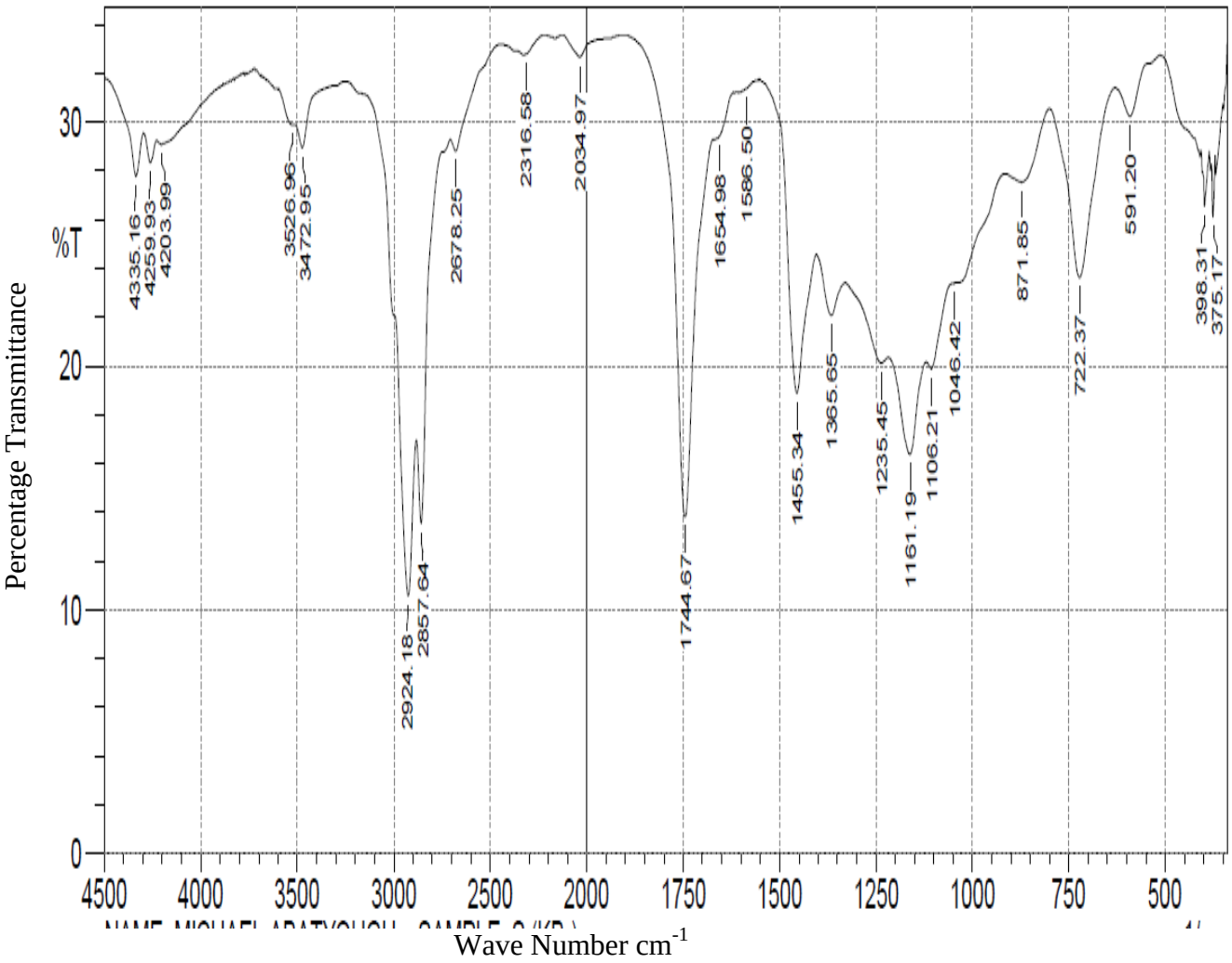


Figure 4. 10: Fourier transformed infrared spectra of biodiesel catalysed by $AlCl_3$

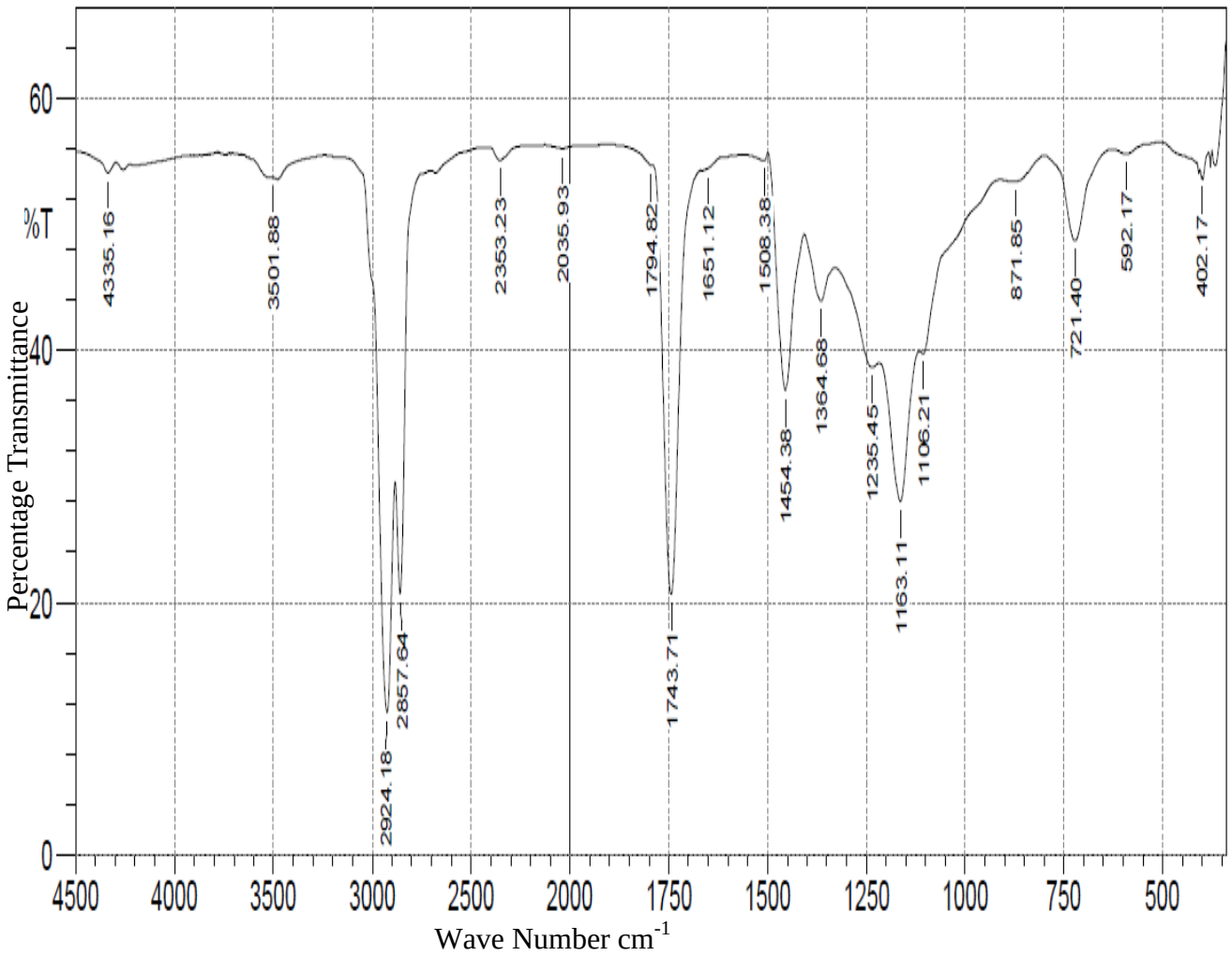


Figure 4. 11: Fourier transformed infrared spectra for biodiesel catalysed by NaOH

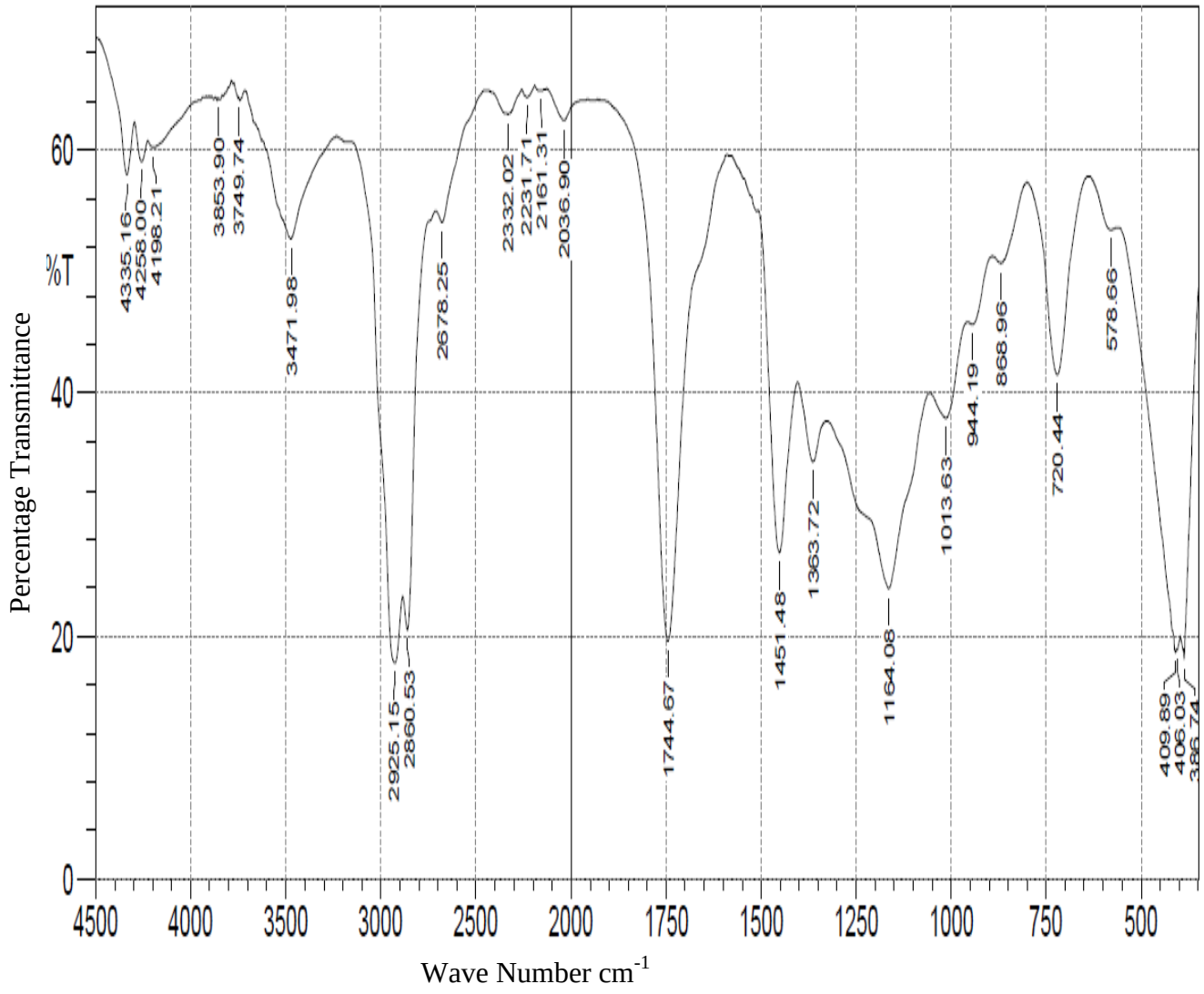


Figure 4. 12: Fourier transformed infrared spectra for biodiesel catalysed by NaOH/CaO

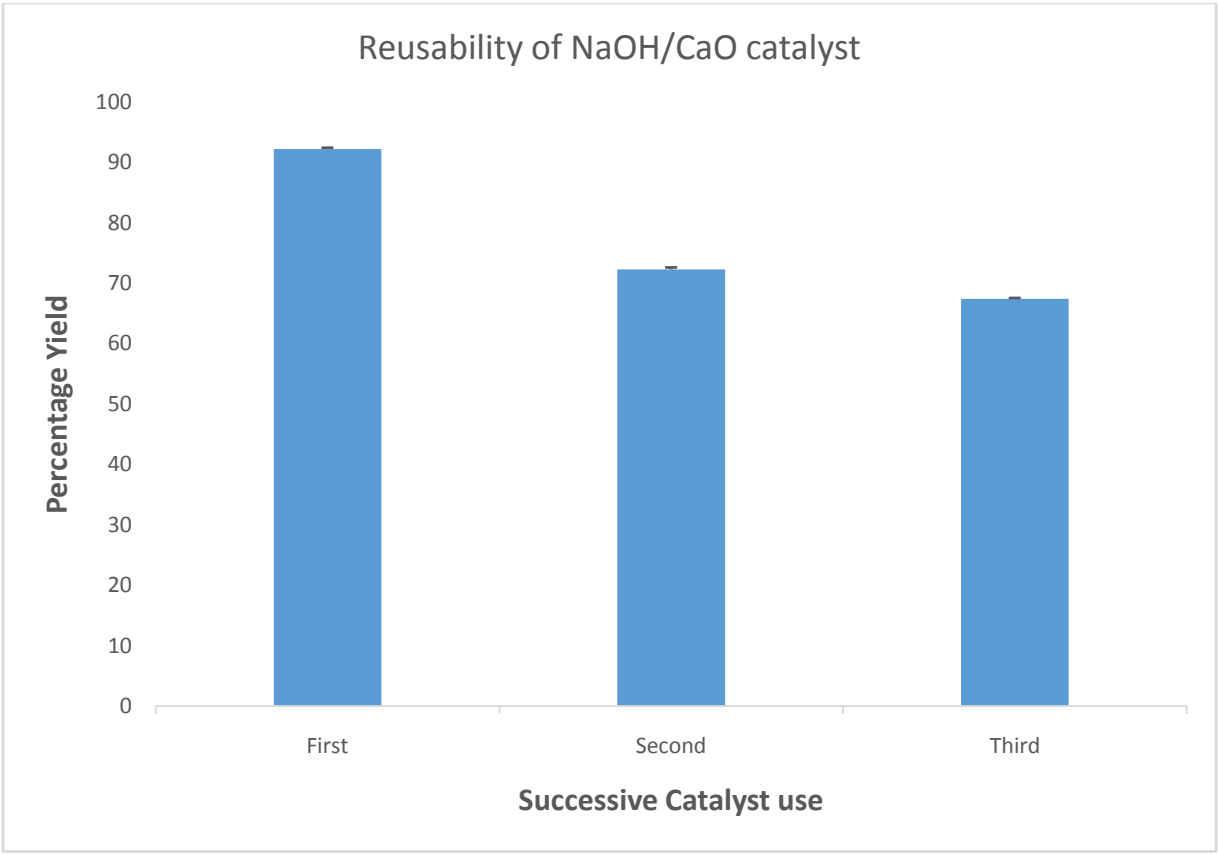


Figure 4. 13: Reusability of NaOH/CaO catalyst and biodiesel yield

CHAPTER FIVE

5.0 Discussion

5.1 Properties of Waste Cooking Oil

5.1.1 Physicochemical properties

Table 4.1 presents the physicochemical properties of the waste cooking oil used in this study.

The high acid value of 3.8±0.74 mgKOH/g which is far greater than the ASTM standard of <0.5 for biodiesel feedstock suggests that the oil will require esterification before it can be transesterified into biodiesel. Kulkarni *et al.,* (2006) also reported pretreatment for waste cooking oil biodiesel feedstock having an acid value of 5.3 mgKOH/g.

The density of the waste cooking oil was found to be 0.89±0.07 g/cm^3 which is within the ASTM standard of 0.86-9.0 g/cm^3 for density of biodiesel. This is lower than density of 9.21 g/cm^3 reported by sanli *et al.,* (2011)

The viscosity of biodiesel feedstock is reduced after transesterification into biodiesel. Thus, the waste cooking oil viscosity of 18.6±0.36 mm^2/s is above the 1.9-6.0 mm^2/s ASTM standard, this is due to the prominence of palmitic fatty acid and other long chain fatty acids in the oil shown in Table 4.2 (Tat and Van Gerpen, 2000).

Presence of moisture and sediment may lead to saponification during transesterification, the high moisture and sediment content of 3.6 % for the waste cooking oil need to be reduced to <0.05 % as required by the ASTM standard to avoid soap formation and deactivation of catalyst during transesterification.

5.1.2 Fatty acid profile

The fatty acid composition of waste cooking oil determined by Gas chromatography mass spectrophotometer showed the presence of fatty acids of different chain lengths compounds are present in the sample as shown in Table 4.2. The fatty acid profile is one of the key

factors that determine the suitability of any feedstock for use in biodiesel fuel production (Knothe, 2006). For this research, the fatty acid profile of the waste cooking oil (WCO) feedstock had the major fatty acids to be oleic, linoleic, palmitic, myristic and stearic acids, indicating the presence of mono and poly unsaturated as well as saturated fatty acids and also saturated fatty acids. These presence of triglycerides is what makes the oil a suitable feedstock for biodiesel production.

5.1.3 Determination of functional groups

The FTIR spectrum of waste cooking oil (WCO) was carried out in the wave number range of 400 – 4000 cm^{-1} to determine the functional groups present on the waste cooking oil (WCO). The FTIR spectra of the waste cooking oil sample is shown in Figure 4.1 and it indicates the presence of methylene stretch at 2931.90 cm^{-1}. The presence of a broad peak at 1643.41 cm^{-1} – 1737.92 cm^{-1} shows the presence of free fatty acids attatched to the carbonyl group of ester linkages confirming the high free fatty acid content reported in Table 4.1.

5.2 Properties of Carbide slurry and Prepared Calcium Oxide

5.2.1 Determination of functional groups

Changes in the structure of the compounds will be observed through alterations in the infrared spectra (He *et al.*, 2004). A favorable dehydration and desorption is necessary for the preparation of a stable catalyst which is related to surface regeneration process and reactivity. Figure 4.2 show the FTIR spectrum of the carbide slurry and indicate major peaks that are characteristic of inorganic compounds. The spectrum shows the absorption bands at 3540- 3645 cm^{-1} related to hydroxyl group (OH–) stretching mode and the peak at 1437 cm^{-1} correspond to the out of plane bending of CO_3^{2-} groups (Liu *et al*., 2010). The FTIR spectrum of prepared calcium oxide is shown in figure 4.3, the strong band at 3450-

3513cm^{-1} corresponds to the O–H bonds from the remaining hydroxide or from water molecules on the external surface of the samples during handling to record the spectra (Ghiasi and Malekzadeh 2012). The broad band at 1438 cm^{-1}, as well as a weak band at 880 cm^{-1} indicates the C–O bond related to carbonation of CaO particles. The strong band at 465 cm^{-1} identified vibration of the Ca–O bond thus producing more basic sites due to CaO that are essential for trans esterification to occur (Tangboriboon *et al*., 2012) There is a tiny dip in the spectra at 2340 cm^{-1} this may be due to the presence of atmospheric CO_2 .

5.2.2 Scanning electron microscopy (SEM) studies

Plates 4.1 and 4.2 show the SEM surface morphology of the carbide slurry and calcium oxide respectively. The carbide slurry (Plate 4.1) show massive, aggregated morphology, and in some instances, there are some bulky flakes. It is also observed that the prepared calcium oxide showed a more heterogeneous agglomeration in terms of dimension and particle size (polydispersity), comprising many particles of varying sizes and properties this may be due to the interactions. These results are in agreement with the findings of Engin *et al.*, (2006). where calcium oxide was prepared from egg shells. The shells displayed a typical layered architecture, when the calcination temperature was increased from 700 to 1000°C. The microstructures of shells were changed significantly from layered architecture to porous structure (Hu *et al*., 2011). In this study, it is of importance to note that the prepared calcium oxide show significant change in morphology compared to the carbide slurry. These observations support the FTIR data indicating that at high temperatures, the curved plates in the carbide slurry transforms to flat layers showing that not only the basal spacing but also the morphology of the compound depends on the density and type of particles within the interlayer space.

5.3Optimization of Esterification of waste Cooking Oil

Response surface plots shown in Figure 4.4 shows the interaction between reaction time (hr) and catalyst weight against percentage free fatty acid reduction (% FFA reduction). The reduction is seen to increase significantly at initial time, but insignificant change was observed for reaction time above 2 hr. Theoretically, adequate reaction time enhanced the esterification reaction since at higher time mass transfer rates among the reactants is accelerated as the molecules gained more kinetic energy, and collided more, eventually leading to higher conversion in a shorter period (Park, 2010). The same trend in this experiment was also reported by Elsheikh *et al.,* (2011) in esterification of crude palm oil using (1-butyl-3-methyl-imidazolium hydrogen sulphate) ionic liquid [bmim]HSO4] to catalyze the reaction, the conversion of FFAs remained virtually the same after reaction time of 2 hr, however, there was slight decrease in the conversion after 6 hr of reaction in this study. Leung *et al.,* (2006), mentioned that conversion of FFAs was related to the reaction time, where prolonged time favored the backward reaction (i.e. hydrolysis of esters), which reduced the conversion.

Response surface plot for interaction between catalyst (wt %) and methanol-oil molar ratio against % FFA reduction is illustrated in Figure 4.5. The conversion increased rapidly exceeding 82 % for molar ratio of 6.0 regardless of any catalyst load. Catalyst loading of 2 wt % had the highest impact on acid conversion. However, the effect of water produced during the esterification reaction significantly affects the process which could be improved by water removal in the mixture continuously (Ghadge and Raheman, 2006). The interaction between time and molar ratio shown in Figure 4.6 indicates a decrease in percent reduction of FFAs with increasing time and a gradual increase in it's conversion with increasing molar ratio of methanol to oil. This could be as result of mass transfer limitations (Yeong and Park, 2009) .

The main effect interaction of factors is shown in Table 4.4 and explains the contributions of individual and combined factors to the percentage reduction of FFA. Time and molar ratio proved to be equally important with 15 % contribution respectively. The highest influence of 51 % was observed for the interaction of reaction time and catalyst weight. Generally the factors can be said to have a positive interaction and this accounts for the 91 % highest FFA reduction recorded on run five (5) of the design of experiment.

Response surface plots shown in Figure 4.7 show the interaction between methanol–oil molar ratio and reaction time (hr) against % FFA reduction. The free fatty acid reduction is seen to increase significantly at initial time, and a drastic increase was observed from reaction time above 1.97 hr. Leung *et al.,* (2006), however, mentioned that conversion of FFAs was related to the reaction time, where prolonged time favored the backward reaction (i.e. hydrolysis of esters), which reduced the conversion.

The interactions between reaction time (hr) and catalyst load (wt %) against % FFA reduction is shown in Figure 4.8. The reduction was highest at higher time and higher catalyst weight, attaining close to 80% reduction of free fatty acid while the plot for interaction between catalyst (wt %) and methanol-oil molar ratio against percentage free fatty acid reduction is illustrated in Figure 4.9. The conversion increased steadily with increasing molar ratio exceeding 75 % for molar ratio of 5.50 regardless of any catalyst loading before steadying. Catalyst loading of 5 wt % had the highest impact on free fatty acid reduction with a drastic increase in reduction from beginning to finish. However, the effect of water produced during the esterification reaction significantly affects the process which may hinder the catalytic activity (Ghadge and Raheman, 2006).

The main effect of interaction of factors shown in Table 4.6, and it shows that the interaction of methanol-oil molar ratio and reaction time had the highest influence 16.46 % for the combined effect. The three factors together had 20.98 %, while the lowest influence

of 4.95 % was for the interaction between catalyst loading and reaction time. Catalyst weight can be said to be the most influencing factor with 26.05% contribution.

5.4 Yield of Biodiesel

The produced biodiesels, recorded appreciable yields owing to the fact that most of the free fatty acids have been stripped off by optimizing the esterification process. The percentage yields of produced biodiesels ranged from 90.2±0.57% for $AlCl_{3,}$ 89.7±0.16% for NaOH and 92.2±0.31% for NaOH/CaO catalyzed biodiesels. A lower yield was observed for the alkali catalyzed biodiesel, this may be as a result of water and soap formed during transesterification process. Chung (2010) while transesterifying *Vemicia fordii and Camellia japonica* seed oils with methanol using alkaline catalysts reported that water and free fatty acids produced soap and deactivated the catalyst thereby reducing the yield to only 76% conversion. Additionally, Soriano *et al*. (2009) studied transesterification of canola oil to produce biodiesel via homogeneous Lewis acid ($AlCl_3$) as catalyst and reported high yields of biodiesel up to 90% owing it to the high acidity of $AlCl_{3.}$ Similarly 90% biodiesel yields with CaO and its co-impregnates have been reported by Liu *et al.*, (2008) in his study on producing biodiesel fuel from soybean oil using CaO as a solid base catalyst. The authors reported that besides the fact that the presence of water in the process has little effect on the catalyst, the use of CaO as a catalyst could provide many advantages such as: high activity, lengthened catalyst life and moderate condition of reaction.

5.5 Physicochemical Properties of Biodiesels

The physicochemical properties of the biodiesels are shown in table 4.7, they are used to access the quality of the fuels they include:

5.5.1 Acid value

Acid value is a measure of the number of acidic functional groups in a sample and is measured in terms of the quantity of KOH required to neutralize the sample (Cvengros,

1998). The biodiesel samples in this research showed Acid values of 0.12±0.21 mg/KOH/g for $AlCl_3$,0.26±0.10mg/KOH/g for NaOH and 0.18±0.24 mg/KOH/g for NaOH/CaO biodiesel samples as shown in Table 4.7.

The acid value for NaOH/CaO catalysed transesterification was less than that catalyzed by NaOH, this could be due to incomplete transesterifcation as a result of water and soap formation with NaOH catalyst , while the slightly lower value for $AlCl_3$ may be due to the lack of interfering effects since same catalyst was used in the esterification and transesterification processes with little water formed. The standard limit in the European norm is < 0.5 mg KOH/g sample, whereas the American standard testing methods, allows slightly higher values of <1% FFA (meher *et al.,* 2006). In 2006, the ASTM D 6751 biodiesel acid-number limit was harmonized with the European biodiesel to a value of 0.50mg KOH/g. (Mahajan *et al*., 2006). Lang *et al*. (2001) reported that the acid values of the ethyl esters of linseed oil, canola oil, sunflower oil and rapeseed oil were 0.884, 0.869, 0.876 and 0.873 mgKOH/g, respectively. Therefore the acid values of the biodiesel samples produced in this study, falls within acceptable standard. The acid value can also be improved by controlling the trans-esterification, washing and drying processes.

5.5.2 Saponification value

The saponification value indicates the ability of the oil to make soap. High saponification value indicates that the oils are normal triglycerides and very useful in soap manufacture industry. The saponification values (SV) of the biodiesel samples are in the range of 190.66±0.44 - 205.29±0.35, with $AlCl_3$catalyzed biodiesel having the highest value of 205.29±0.35, this could be due to the formation of water and reaction of the catalyst with residual free fatty acids. All the values were within the ASTM limits. Kulkarni *et al.,* (2006), reported saponification values ranging from 184-194 for various biodiesel samples from waste cooking oil.

5.5.3 Density

Density is a key fuel property, which directly affects the engine performance characteristics. Many performance characteristics, such as cetane number and heating value, are related to the density (Tat and van Gerpen, 2000). Fuel density affects the mass of fuel injected into the combustion chamber and thus, the air-fuel ratio. This is because fuel injection pumps meter fuel by volume not by mass and a denser fuel contains a greater mass in the same volume. Thus, the changes in the fuel density will influence engine output power due to a different mass of fuel injected (Alptekin and Canakci, 2008). Density limits in the European EN norm (standard) are in the range of 860-900 kg/m³ (meher *et al.* 2006). In many studies, it was observed that biodiesel's density did not changed much, because the densities of methanol and oil are close to the density of the produced biodiesel (Graboski and McCormik, 1998; Encinar *et al*., 2005). The densities of the produced biodiesel samples are shown in Table 4.7. The trend in the densities was 0.88±0.28> 0.86±0.31>0.86±0.35 g/cm^3 for transesterifications catalyzed by $AlCl_3$ >NaOH>NaOH/CaO respectively. The density of the waste cooking oil wasfound to be 0.89±0.07 g/cm^3, this could be due to presence of free fatty acids in the oil. Generally, the density of oils decreases with molecular weight yet increases with unsaturation level (Gunstone, 2004). Tate *et al*. (2006) reported that density is a function of temperature and decreased linearly for canola methyl esters, soy methyl esters, and fish oil ethyl esters by 1.23 kg/m^3, for temperatures between 20–300 ^{o}C. Densities of biodiesel fuels are generally higher than those of petrodiesel, however, the energy content of biodiesel is lower both in mass and volume basis compared to diesel fuel (Canakci and van Gerpen, 2001).

5.5.4 Cloud point and pour point

Cold flow properties of biodiesel samples from the NaOH/CaO prepared catalyst in this experiment were within ASTM acceptable limit as shown in Table 4.7. Same observation

was made for both $AlCl_3$ and NaOH catalysed transesterification reactions. Generally, levels of saturation of the various biodiesel samples might be responsible for the observed cloud points (CP) and pour points (PP) of 10.0±0.53 and 6.0±0.36, 11.0±0.62 and 6.0±0.25 and 12.0±0.49 and7.0±0.47 for $AlCl_3$, NaOH and NaOH/CaO catalysed transesterification reactions. Petro-diesel has cloud point standard range of -15 to 5 ^{0}C, and pour point standard range of -35 to -15 respectively, whereas biodiesel has much higher CP and PP standard values (meher *et al.*, 2006). Tansesterification does not alter the fatty acid composition of the feedstocks, therefore, biodiesel made from feedstocks containing higher concentrations of high-melting point saturated long-chain fatty acids tends to have relatively poor cold flow properties (Dunn, 2005).

5.5.5 Cetane number

Cetane numbers (CN) are the indicators of ignition properties of the diesel fuel. The higher the cetane number, the more efficient the ignition, because of the higher oxygen content. The Cetane number of a diesel fuel is a relative measure of the interval between the injection of the fuel into the cylinder and the onset of auto-ignition, i.e. the ignition delay (ID) time. The shorter the ID time, the higher the Cetane number and vice versa. Fuels with low cetane numbers tend to cause diesel knock and show increased gaseous and particulate exhaust emissions because of incomplete combustion (Knothe *et al*., 1998). Biodiesel has a higher cetane number compared to petroleum diesel. The cetane numbers of waste cooking oil biodiesel is shown in Table 4.7 and were found to be 56.0±0.58, 61.0±0.33, and 64.0±0.27 for $AlCl_3$, NaOH and NaOH/CaO catalysed transesterification reactions respectively. These are within ASTM acceptable limits and can be seen to increase with degree of saturation. The standard ASTM D975 for conventional diesel fuel requires a minimum CN of 40, whereas the standards for biodiesel prescribe a minimum of 47 (ASTM D6751) or 51 (EN14214), (Knothe, 2005). The cetane number of the biodiesel

samples are within acceptable limits and agrees with reports by van Gerpen, (1996) and Knothe *et al*. (2003) who reported that feedstocks that are high in saturated fatty esters has a high CN, The oxidative stability of biodiesel fuels also increase with level of saturation, However, the drawback of high amount of saturated fatty compounds in biodiesel fuel is that the cold filter plugging point occurs at a higher temperature.

5.5.6 Viscosity

Fuels with low viscosity may not provide sufficient lubrication for the precision fit of fuel injection pumps, resulting in leakage or increased wear (Knothe and Steidley, 2005a). Viscosity of biodiesel is about an order of magnitude lower than that of the parent oil as observed in the results presented in table 4.1 (Knothe, 2005b). High viscosity is the major fuel property which explains why neat vegetable oils have been largely abandoned as alternative diesel fuel (Dunn and Knothe, 2001). The difference in viscosity between the parent oil and the alkyl ester derivatives can be used to monitor biodiesel production (Knothe, 2000). Viscosity increases with chain length (number of carbon atoms). This holds also for the alcohol moiety because the viscosity of ethyl esters is slightly higher than that of methyl esters (Knothe and Steidley, 2005). Geller and Goodrum (2000) reported that viscosity of pure and saturated triacyl glycerols of 6:0 to 18:0 correlated with the carbon number in a second order polynomial fashion. The effect becomes more evident at lower temperatures, where the molecular movements are even more restricted. The studied catalysts produced in this work gave viscosities within the acceptable limits as shown in Table 4.7 with $AlCl_3$ catalysed biodiesel having the best fuel viscosity at 2.90±0.19 mm^2/s while NaOH/CaO catalysed transesterification has viscosity of 4.20±0.13 mm^2/s this suggests that transesterification was not complete. Viscosity increases with increasing degree of saturation. Kinematic viscosity at 40 °C is limited to 3.5-5.0 mm^2/s in the European biodiesel standard norms. The American specifications allow a broader range of

values (1.9-6.0 mm²/s) (meher *et al.*, 2006). The corresponding limit for petrodiesel fuel is considerably lower at 2.0 - 4.5 (Knothe, 2006).

5.5.7 Iodine value

The traditional measure of the degree of bonds is given by the iodine value. The higher the iodine number, the more unsaturated (the greater the number of double bonds) is the vegetable oil and the higher is the potential for the vegetable oil to polymerise. The highest iodine value for the biodiesel samples was 124.21 g iodine/g for NaOH/CaO while the lowest was 103.34 g iodine/g for $AlCl_3$. These iodine values can be seen to vary with degree of saturation, with $AlCl_3$ being the most saturated and least iodine value. Hilber *et al.*(2006) reported that the iodine values of rapeseed, corn, soybean, sunflower and waste cooking oil were found to be 104, 94, 103, 97 and 82, respectively. The iodine value can be easily reduced by transesterification of vegetable oil with methanol using sodium hydroxide as catalyst. The methanol breaks the double bond and converts the vegetable oil into more saturated oil which reduces the tendency to polymerise**.**

5.5.8 Flash point

The flash point is the temperature at which the fuel will start to burn when it comes to contact with a flame or hot surface (Ali *et al.*, 1995). It is an important parameter from the safety point of view during storage and transportation. This temperature is correlated with its volatility, which is an important fuel feature for engine starting. The combination of high viscosity and low volatility of a fuel causes bad cold engine start up, misfire and ignition delay (Szybist *et al.*, 2007). A fuel with high flash point may cause carbon deposits in the combustion chamber. The flash point of all biodiesel samples as shown in Table 4.7 are far above that of petro-diesel, reflecting the non-volatile nature of these fuels. Transesterification catalyzed with NaOH catalyst had the highest value of 167 ± 0.51^0C while $AlCl_3$ had the least 158 ± 0.42^0C due to the level of saturation in the various fuels.

Canakci *et al.* (2005) reported that inspite of the fact that the flash points of vegetable oils were reduced through transesterification, they were still higher than those of diesel fuel, regardless of whether the biodiesel was from pure vegetable oils or from waste cooking oil. However, if they are compared with each other, it was seen that the flash points of bio-diesels from waste oils are higher than those from pure vegetable oils since they have relatively more saturated fatty acids in their composition.

5.5.9 Moisture and Sediment

As a result of the hygroscopic nature due to high polarity of fatty acid methyl ester, biodiesel tends to absorb water during the final washing step in the production process and during storage. Free water promotes biological growth which may cause blockage of fuel filters and fuel lines as a result of induction of sludge and slime formation. Also high moisture content is also associated with hydrolytic reaction which partly converts fatty acid methyl esters into free fatty acids which are linked with filter blockages as well (Mittelbach *et al*., 2004). Fuel contaminated with water can cause engine corrosion or react with the glycerides to produce soaps and glycerine. Therefore, <0.05 % of water in fuels is what is accepted in the ASTM standard (meher *et al.*,2006). In this research, the produced biodiesels were routinely dried over anhydrous magnesium sulphate and recoreded moisture contents for the biodiesels prepared using different catalysts shown in Table 4.7. This technique, although used in laboratory practice, is not very efficient; the water content in several samples of the biodiesel was reduced to the accepted levels (< 0.05 %). On an industrial scale, dewatering is usually carried out by distillation under vacuum (0.05 bar) at temperatures of 30–40 ^{0}C. In this experiment. A rotary evaporator was used to remove water and any remaining alcohol after transesterification..

5.6 Fatty acid Methyl Esters (FAME) Profile

The profile of fatty acids show the fatty acid composition of biodiesel samples are similar to the waste cooking oil (WCO) feedstock with a variation in levels of saturation in the biodiesel samples. Table 4.8 shows the fatty acid profile of the biodiesel samples with percentage yields. More levels of unsaturation were observed in transesterification with NaOH/CaO, these would influence the fuel properties of the biodiesel as it will have higher cold flow properties, oxidation and flash point but a lower energy content and density. while $AlCl_3$ catalyzed transesterification had slightly higher levels of saturation. Gaby and Peter, (1997) reported that fatty acid profile of oils affect fuel properties of biodiesels. At high temperature, as such commonly experienced in combustion engines, the peroxidation can be accelerated and engine can quickly become gummed with polymerized fatty acid methyl esters (Mohibbe *et al.,* 2005)**.** This can be compared to Felizardo *et. al.,* (2006) analysis of waste cooking oil biodiesel and showed a high level of unsaturation with linoleic and oleic acid esters having highest compositions respectively-.in order tocompare, Betiku *et al.,* (2013). shows a high level of unsaturation with 76 % unsaturated fatty acid and about 21% with linoleic acid having 52 % composition.

5.7 Determination of Functional group

The FTIR spectra of the biodiesel samples are shown in Figures 4.10, 4.11, and 4.12 for $AlCl_3$, NaOH and NaOH/CaO catalysed biodiesel samples respectively. The changes in the percentage (%) transmission and functional groups showed the modifications that occurred during the transesterification process. In the transesterification of waste cooking oil, the FTIR spectra of the raw oil and biodiesel are very similar because of high chemical similarities that exist among triglycerides and methyl ester at the 2900, 1750 and 1100 cm^{-1}. All biodiesel samples showed the methylene stretch peak at 2800-2900 cm^{-1}. However, small differences are observed as a shift or intensity in the peaks in the other regions (C=O

ester, CH_3 and C-O ester) . The strong ester peak at 1750 cm^{-1} (C=O ester) and at 1170 – 1200 cm^{-1} (C-O ester) are clearly present in the spectra at 1744.67 cm^{-1} and 1161.19 cm^{-1} for $AlCl_3$, 1743.71 cm^{-1} and 1106.11 cm^{-1} for NaOH as well as 1744.67 cm^{-1} and 1164.08 cm^{-1} for NaOH/CaO . This is in agreement with the study of Knothe,(2006) who stated that the wave frequency (cm^{-1}) for (C=O ester) functional group is 1750 – 1725 $cm^{-1}$and indicates a reduction in glycerol and free fatty acids. Outside these two regions, another characteristic peak that indicates the presence of ester group in the mixture of methyl ester can be observed at 1454.38 cm^{-1}. Similar result was reported by (Yun *et al*., 2011; Siatis *et al*, 2006**).**

5.4.5 Reusability of prepared NaOH/CaO catalyst

The reusability of the prepared NaOH/CaO catalyst that gave 92.2±0.31% biodiesel yield, through three transesterification reac-tion cycles of esterified waste cooking oil is shown in Figure 4.14. After the second reaction cycle that gave a 72.3±0.18% biodiesel yield, the catalyst still gave a favourable yield of 67.4±0.09% for the third cycle, though less than the previous yields. This suggests to the fact that adsorption of transesterification reaction products such as residual methyl ester, glycerol, water and oil containing impurities on catalyst surface, may have hindered the interaction of fatty acids and methanol to acidic sites of NaOH/CaO catalyst. The catalytic performance of the spent catalyst can be partially recovered by intensive and sequential washing with methanol and dilute acids (50% v/v). It was also observed that the gradual decrease of biodiesel after each subsequent yield after each reaction cycle was also due to the presence of water which also has an adverse effect on the equilibrium of transesterification reactions. Obtained results suggest that NaOH/CaO catalyst can be a suitable and durable catalyst for successful catalytic transesterification reactions.

CHAPTER SIX

6.0 Summary, Conclusion and Recommendation

6.1 Summary and Conclusion

Waste cooking oil (WCO) from eateries was pretreated and their transesterification with alkali supported calcium oxide, prepared from welders wastes gave good fatty acid methyl ester (FAME) yield and fuel quality. The FAME sample thus obtained, was then compared with FAME prepared from conventional homogeneous alkali catalyst (NaOH), heterogeneous$AlCl_3$catalystand acceptable standards. The results of the physicochemical analysis showed good quality fuel with variation among the catalyst type used,while the chemical composition of CaO monitored using FTIR indicated presence of Ca-O band at the 400-500cm^{-1} .

Physicochemical and methyl ester profile of waste cooking oils and their corresponding esters from various catalysts have been analysed by GC-MS, FTIR and ASTM methods. A gradual decrease in acid value was observed from waste cooking oil, esterified and transesterified methyl esters, due to loss in weight from free fatty acids and glycerol. Generally the methyl ester profile showed variation in levels of saturation, this effect is seen in the various fuel properties for cloud and pour point, cetane number, iodine number and oxidative stability for $AlCl_3$,NaOH and NaOH/CaO catalysed biodiesels. Reasonable yields of biodiesel were also obtained using the prepared catalyst up to the fourth cycle use.

Based on results of this study, it can be concluded that; It is possible to lower the cost of biodiesel by using readily available waste materials, this will help sanitize our environment as millions of tonnes of these wastes are generated annually. Also, alkali surported on CaO prepared from welders slurrycan be a suitable catalyst for biodiesel production as it competes favourably with conventional heterogenous and homogenous catalysts.

6.2 Recommendations

It is recommended that:

- Catalytic activities of the prepared NaOH/CaO catalyst in biodiesel synthesis should be tried on other oil sources.
- The prepared CaO from waste welder's slurry should be optimized as solid support for other catalysts
- The quality and yield of biodiesel prepared using NaOH/CaO catalyst should be optimized experimentally.

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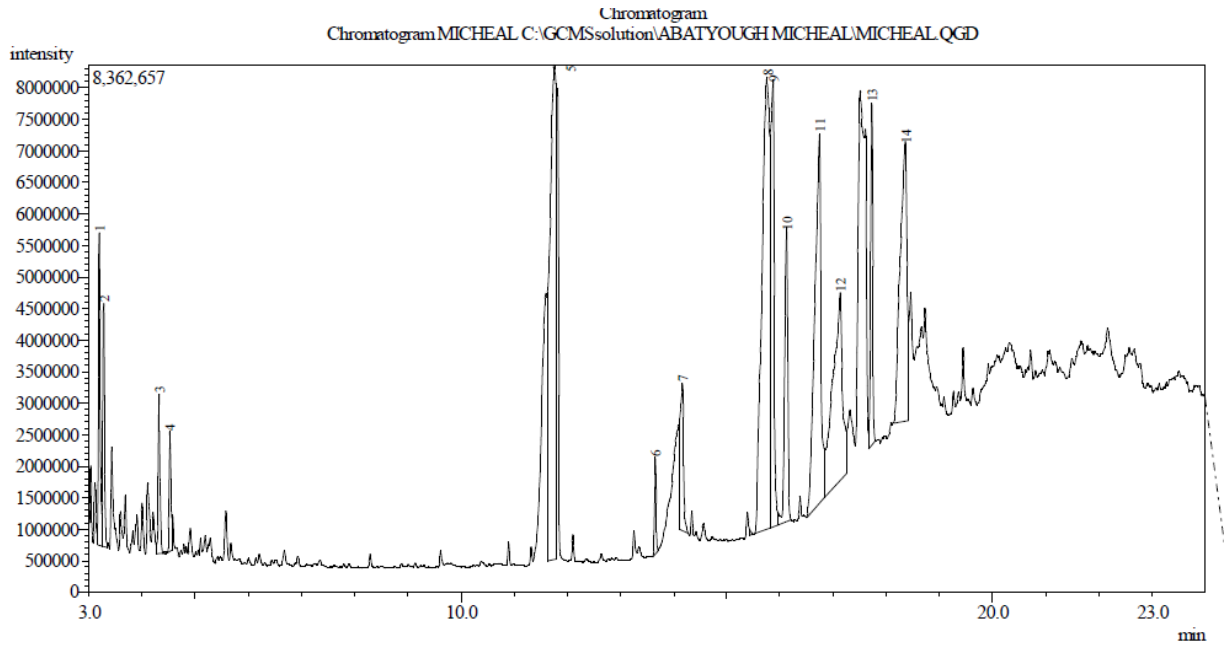
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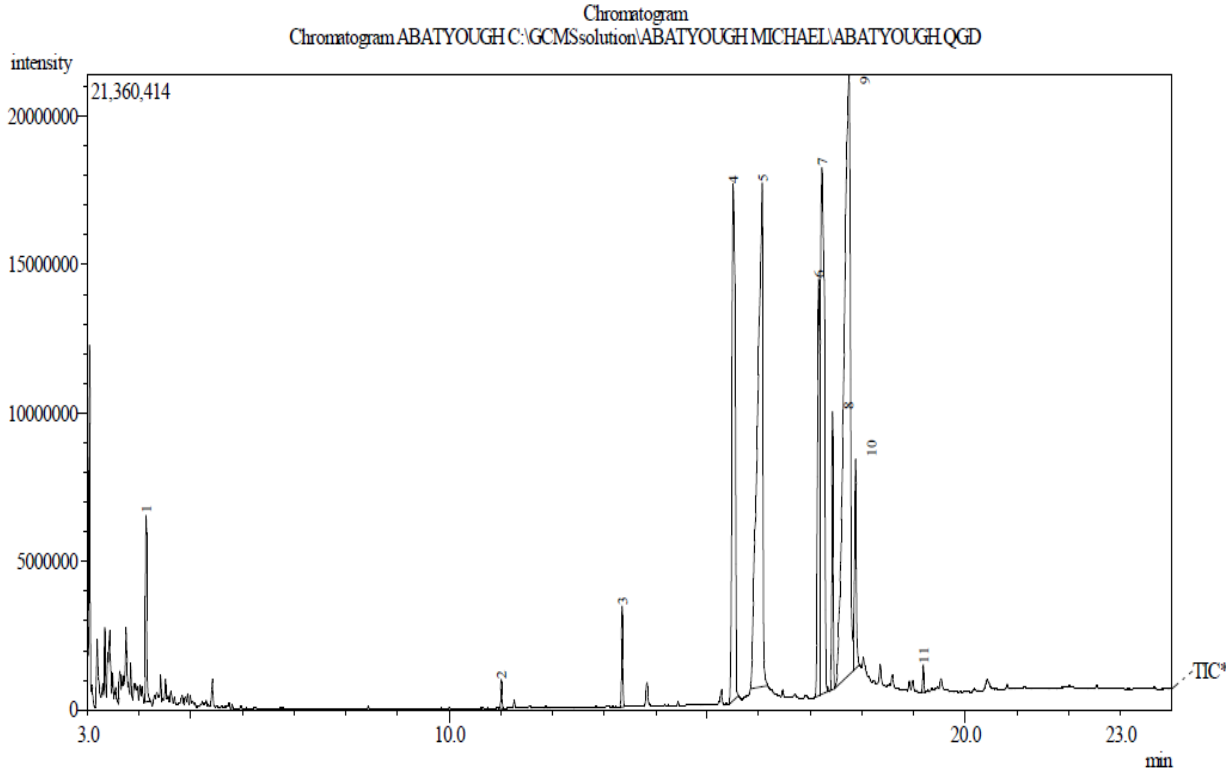
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APPENDICE

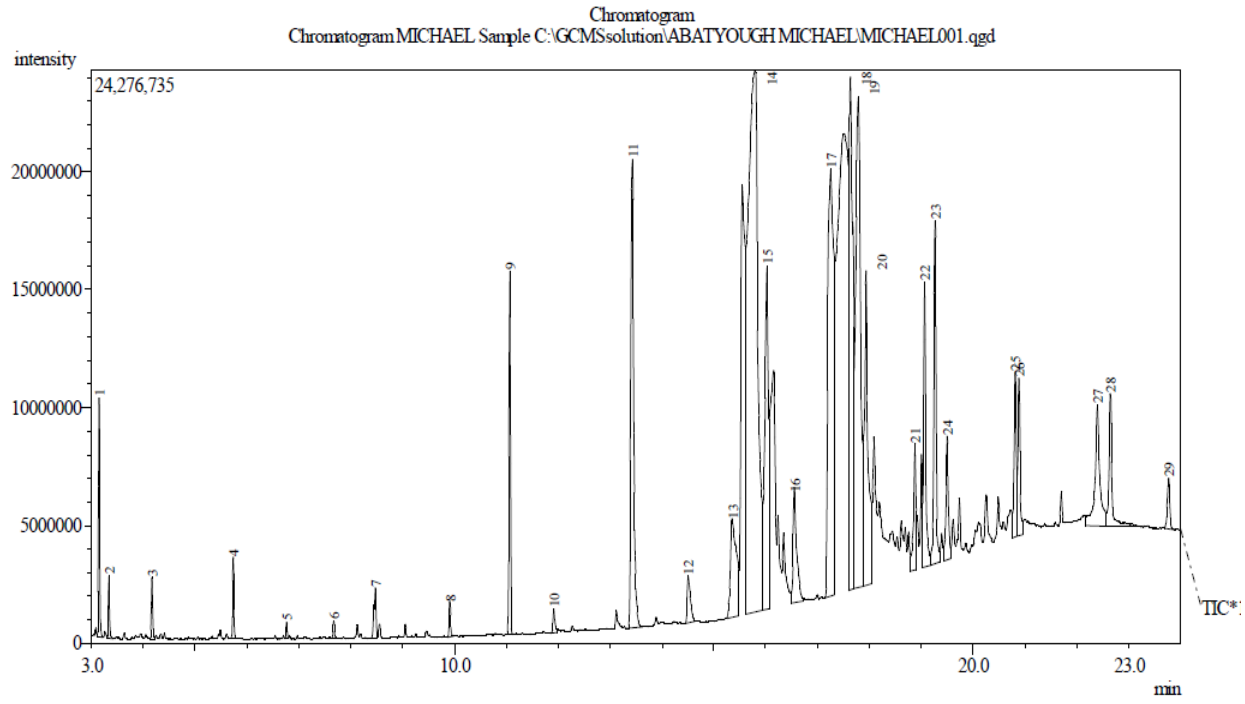
Appendix 1: GC-MS Spectra of waste cooking oil (WCO)



Appendix 2: GC-MS Spectra of NaOH/CaO catalysed biodiesel.



Appendix 1: GC-MS Spectra of $AlCl_3$ catalysed biodiesel.



Appendix 3: GC-MS Spectra of NaOHcatalysed biodiesel.

